ABSTRACT

Title of Document: AN ASSESSMENT OF THE USE OF FLAME RETARDANT PLASTICS FOR MUSEUM APPLICATIONS

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Directed By: Frederick W. Mowrer, P.E., Associate Professor, Ph.D., Fire Protection Engineering

Halogenated flame retardant plastic sheeting may help to reduce the spread of flame in museums; however, the plastics contain chemicals that may be harmful to museum objects in situ, particularly metals. This study assesses historical and contemporary problems and benefits associated with flame retardant plastics with respect to museum applications. This issue was addressed by pairing statistical data on museum fires with standard and novel methods for assessing corrosivity, while also creating a format for future assessments of fire-safety related practices as they are applied in museum settings. Flame retardant plastics were found to cause small rates of corrosion in copper, approximately 1.2 milli-inches per year (mpy), compared to pure polyethylene which corrodes at approximately 0.83 mpy. Conventional testing methods show that flame retardant plastics can be considered safe for limited museum use and that they delay ignition from small heat sources, but they must be assessed for each individual scenario.

An Assessment of the Use of Flame Retardant Plastics for Museum Applications

By

Danielle Leikach

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Advisory Committee:
Professor Frederick W. Mowrer, Ph.D., Chair
Professor Peter B. Sunderland, Ph. D.
Dr. Lynn B. Brostoff, Ph. D., Smithsonian Institution

Dedication

This work is dedicated to the many individuals who have planted the seeds of the ideas behind this endeavor and helped it to grow, and to my family who has always believed in me and has helped me to believe in myself.

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Chapter 1 Introduction

1.1 Background

At the Smithsonian Institution, preservation of the museums' collections is of principal concern. This implies that preventative conservation measures will be taken and these measures "…should be able to identify and quantify all risks to a collection or set of collections [1]." The Museums' collections often include irreplaceable, priceless items, thus the focus is on keeping the collections intact and safe and free from damage or degradation. There are many potential risks that could damage a collection or artifact, such as physical force, fire, water, criminals, pests, contaminants, light and UV radiation, temperature and humidity.

While collections and objects on display receive a great deal of attention regarding their preservation, it is also interesting to consider objects in storage. Recently, an article appeared in the Washington Post discussing the conditions of the Smithsonian Institution's Freer and Sackler's storage areas [2]. The article stated that the museum buildings urgently needed repair and mentioned that "leaks in Freer and Sackler's storage areas threaten their collections [2]." The spokeswoman for the Smithsonian explained that the potentially vulnerable artworks are protected by plastic. The plastic being used in the storage areas is pure polyethylene sheeting, only a few milli-inches thick. To a conservation scientist, plastics are not necessarily the safest materials for collections, although pure polyethylene is considered to be a "safe or stable material [3]." The main risk factor from a plastic is considered to be contaminants, including the gases and vapors emitted from the storage materials, as well as plasticizers, which migrate to the surfaces [1].

This use of plastic sheeting takes place in many museum storage facilities, as plastic sheets protect stored items from both moisture and dust. Large rolls of plastic sheeting are stored in the same area as the collection in storage.

From the perspective of a fire protection engineer, a storage area where many flammable objects are densely packed presents an elevated risk for the spread of fire. The addition of protective plastics adds to the fuel load and may increase the risk of ignition. It has been the desire of the Smithsonian's fire protection engineers to switch over to flame retardant treated plastics for a long time, but the conservation scientists and curators have resisted, stating that not enough is known about the treated plastics. Any additives present the possibility of corrosive or other damaging properties to a material, and so that it is considered potentially dangerous to expose collections in storage to these materials for extended periods of time.

Plastic sheeting may also be used in the instance of renovations in both museums and storage spaces. Though there are generally stringent guidelines regarding the use of plastics in the presence of welding and hot work, if there is a large supply of untreated and unrated plastic available, this material might be used to protect any remaining objects or for creating dust barriers. For small maintenance tasks, this same scenario might occur. In the case of the Smithsonian, this is highly unlikely because the fire protection department meticulously plans out all the aspects of fire safety and protection involved in any renovation or building project. However, many smaller museums do not have a department devoted to fire protection and so it is possible that these important considerations will be overlooked.

The Smithsonian Institution is a leader not only in conservation and conservation science, but also in the development of enhanced fire protection in museum applications. The rigorous guidelines set out by codes and standards are met and often exceeded with meticulous care. The Smithsonian's approach to fire protection has been a paradigm to other institutions across the country and around the world. Although the fire protection department plays a significant role in maintenance, new construction and new exhibits at the Smithsonian's facilities, it is often difficult to find a balance between long-term preservation of collections and the less frequent need for fire protection.

While water and structural damage can often be repaired, and stolen property can sometimes be recovered, fire can cause damage that is permanent and irreparable. It is a threat that cannot be removed, no matter how many precautions are taken, but the risk can be reduced by controlling ignition points and fuels. According to a paper presented by the Smithsonian's Assistant Director of fire protection and safety, J. Andrew Wilson, interior finishes that can be ignited with a match should never be used [4]. The paper stipulates that exhibits should be constructed of fire safe materials, ensuring that all materials used are fire retardant to reduce risk to collections and the building [4].

Despite a name that implies a fireproof material, flame retardant plastics will burn. Fire retardant treated plastics are still added fuel load, and if exposed to enough heat, they will burn, potentially releasing chemicals that are more toxic and corrosive than fire products from a pure, untreated substance. The likelihood of a fire occurring is relatively small and in the case where a fire does occur, smoke and water are likely to do the most damage to a collection in storage if the fire is controlled.

Flame retardant plastics would better be called ignition or flame resistant plastics because when exposed to small flames or sparks they will not easily ignite. If ignition is achieved, the flame will self extinguish very rapidly. On the other hand, a thin polyethylene flexible tarp will ignite immediately, and the flame will sustain until all the plastic fuel is consumed. In terms of controlling the threat of ignition and the spread of a fire, fire retardant plastics may present a good option if the exposure threat is sparks or small flames.

In order to achieve flame retardant properties in plastic, the most widespread approach is to combine brominated compounds with an antimony oxide synergist [5]. The main group of chemicals used to give the plastic sheets their fire retardant characteristics are polybrominated diphenyl ethers (PBDEs), in Figure 1.1-1.

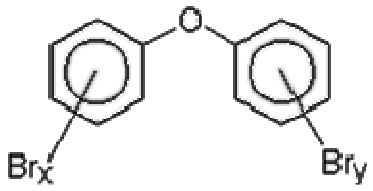


Figure 1.1-1. Polybrominated Diphenyl Ether Molecule (PBDE)

PBDEs are actually a family of chemical compounds consisting of 209 different substances called congeners which differ in the number and position of bromides [6]. For polyethylene plastics, DecaBDE is generally used, meaning that the molecules have 10 bromines. This molecule, shown in Figure 1.1-2, is believed to be more stable than some of the other congeners, and is therefore commonly used in commercial FR materials.

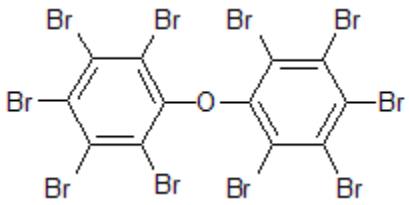


Figure 1.1-2. Decabromodiphenyl Ether Molecule (DBDE)

There is ongoing debate discussing the environmental safety of PBDEs. The lower brominated PBDEs (having 1-5 bromine atoms) are regarded as more environmentally dangerous because they are smaller and more easily absorbed into living organisms, but the higher brominated PBDEs are thought to be more stable and safe. However, many studies are being conducted to determine if larger molecules, like DBDE, are debrominating and how this is affecting the environment [6].

When brominated flame retardants burn, they release gaseous hydrogen bromide (HBr), which is a corrosive and powerful sensory irritant. In terms of life safety, carbon monoxide (CO) and hydrogen cyanide (HCN) are generally the irritant gases that cause rapid incapacitation, while the amount of HBr present is considered to be non-threatening in comparison [7]. In the case of museum storage, life safety is often secondary to property losses, which could be exacerbated by the highly reactive and corrosive HBr gases. However, if a fire is consuming large quantities of the flame retardant plastics, it is already big enough to burn the museum property, and some corrosion would be better than a pile of ashes.

The goal of this research is to evaluate whether or not the use of flame retardant polyethylene plastics in museums is worthwhile by performing a comprehensive risk assessment. This will be examined in three ways: through examination of statistical data from past fires in museums and historical structures and storehouses, through analysis of

damages imparted to museum objects by normal exposure, and through investigation of the burning characteristics of the treated and untreated plastics. To assess the damage from normal exposure, flame retardant plastics and a pure polyethylene sample were tested to determine corrosion incurred by metals due to exposure to the plastics. To assess the burning characteristics, small-scale burn tests using a mock artifact were performed for each plastic.

Using the collected body of data, it is possible to weigh the positive and negative effects of the fire retardant treated plastics on the collections in a museum. This research will also provide a plan for looking at the use of fire retardant treated materials in museums and libraries, as well as any other locations were preservation is of importance.

Aside from fire-related research, this work will help the Smithsonian Institution to investigate alternative material testing techniques. The "Oddy test" is the method currently used to determine the corrosivity of a material to be used in the displaying of a collection [8, 9]. The Oddy test exposes small metal coupons to the material in question and simulates environmental conditions, using an accelerated aging process. The metal coupons act as canaries which are susceptible to visible corrosion from exposure.

The Oddy test is subjective and time consuming, and there are many aspects that are difficult to control. In industry, electrochemical testing has been used to measure corrosion rates in metals when exposed to possible corrosive agents for extended periods of time. As proposed bu C. Reedy, et al., the procedures involved with these tests can be performed much faster than an Oddy test and provide data that allows for calculation of rates of corrosion [10]. Such a test could provide rapid answers to the question of corrosivity of a material in a much more repeatable and objective manner. When

equipped with the correct instrumentation, namely, a Potentiostat device and an electrochemical cell, this test could be an excellent answer to the problematically subjective Oddy test for determining the safety of materials in conservation.

Along with investigating new test methods for assessment of materials used in proximity to art and artifacts, this thesis will provide valuable knowledge to conservation scientists about fire retardants. In many cases, conservation scientists come across chemicals on objects which are difficult to identify. There have been findings in which these chemicals were actually applied as fire retardant coatings or additives, but the literature about fire retardants was not available. By analyzing the effects and reactions of chemical components of fire retardants in fire and normal exposure conditions, new information will be available to conservation scientists for their investigations.

Another important aspect to consider is that the plastic sheeting may not be the only material that contains flame retarding additives in a museum. It is likely that many other display and general construction materials, such as curtains, carpets, woods, etc., are treated with flame retardants, and the volatiles these chemicals may be contributing to an interaction with museum collections. Information gained in this work about the effects of flame retardants may spur questions about other materials used in museums, including the entire museum structure and its furnishings.

1.2 Fires in Museum, Historic Structures and Historic Storehouses

1.2.1 Past Fires

Not all museum fires cause great property damages, but such fires still occur regularly throughout the country and the world. To name a few, in early June, 2007, a fire occurred in Sturbridge, MA at the Old Sturbridge Village, a living history museum.

The fire is believed to have started when a hot ember from the fireplace, used the daily in cooking demonstrations, spread the fire in the kitchen. No artifacts were destroyed by the fire but the fire caused $50,000 in damage. In Early May of the same year, a fire in a replica Huron Ouendat Indian Village the Huronia Museum in Midland, Ontario caused at least $250,000 in damage.

The portion of a museum open to the public does not necessarily hold the entire collection of artifacts and historical objects that a museum may own. Large storage facilities, either off- or on-site, often hold the majority of a museum's collection and are therefore at risk for even greater losses. A fire in a large, open storage facility might completely destroy an entire collection, not only from the fire, but smoke and water damage associated with a fire. In its Annex B, the 2005 edition of NFPA 909, Code for the Protection of Cultural Resource Properties – Museums, Libraries, and Places of Worship, the lack of adequate compartmentation is listed as one of the main reasons fires are able to spread through these types of buildings [11].

As discussed earlier in the case of the Freer and Sackler storage areas, plastic sheeting is used as protection against everyday damage from moisture and dust. Plastic sheeting in storage areas needs to be considered when considering how a fire might spread through a storage area and the fuels present. Plastic sheeting is generally purchased in bulk, where more plastic is acquired than is immediately needed. The unused and sizable rolls of plastic may sit in storage with the collections or in gallery renovation work areas.

It is significant to note that many fires in museums take place during renovations operations where both plastic sheeting and hot work operations are used. According to

the 2005 edition of NFPA 909, the occurrence of fires during renovation, when plastic sheeting is likely to be present, is often increased. The fourth major cause of structural fires in US museums and art galleries is open flame, ember, or torch. The first, second and third causes for fire in US museums and art galleries are electrical distribution, arson, and "other equipment" in third.

On August 31, 2000, a fire occurred in one of the open first floor galleries at the National Air and Space Museum. Hot work activities were being performed on the skylight roof area above the gallery, and slag from the operation fell through an opening in the work platform. The slag fell 60 feet, igniting polyurethane foam being used for impact protection below. Fire retardant plastic sheeting had also been employed in the area of ignition as a dust and moisture barrier. The fire retardant plastic melted away, but performed extremely well and did not appear to continue to burn or propagate the fire in an outward or upward path. The investigation following the fire showed that the foam, which was not flame retardant and had not been submitted for review or approval from the authority having jurisdiction, was the chief factor responsible for the growth of the fire, while the flame retardant plastics had helped to slow the propagation of the flames.

Fire cannot be completely prevented in any setting, but every attempt to slow its spread can mean the difference between catastrophic losses and minor damage. The fire at the National Air and Space Museum was not necessarily stopped because of the presence of flame retardant plastics, but its spread was certainly slowed. If the plastic had not been flame retardant, this minor fire could have caused far more damage and many one-of-a-kind historical artifacts could have been damaged.

1.2.2 Statistical Data

The 2005 edition of NFPA 909 Code for the Protection of Cultural Resources Properties - Museums, Libraries, and Places of Worship includes statistical data regarding the occurrences and causes of fires in cultural resource properties [11]. From 1980-1999 an average of 86 museum fires occurred in the U.S. per year, resulting in an average loss of $1.9 million in property damage. From 1994-1998 an annual average of 61 structure fires per year occurred in museums and art galleries, totaling a loss of $1,255,000 per year in direct property damage. Recent trend suggests that fire losses have been reduced since 1999[11].

According to proceedings from the 1999 National Conference on Cultural Property Protection, "fires are the single greatest cause of property loss in cultural facilities [12]." The paper asserts that the US averages over 100 museum fires each year, with annual property losses exceeding $2 million. These numbers are slightly larger than those provided by the NFPA 909 data, which is based on national estimates provided by National Fire Incident Reporting System (NFIRS) and NFPA survey. The larger estimates are expected to be more accurate because not all fires and losses are reported. Fires are described in this way because of the general destructiveness involved. While aging and deterioration are constant problems occurring over the course of many decades, the sweeping span of a fire can destroy multiple collections in a few hours. Damage from the fire can completely consume museum objects, but smoke and water damage can reach areas within a structure that the fire may never touch.

According to NFPA's study of annual averages of fires from 1994-1998, the most significant causes of fires in museums and art galleries were electrical distribution

equipment (30.4%), other equipment (16.0%), cooking equipment (10.9%), heating equipment (9.0%), open flame, ember or torch (8.6%) and intentional (7.3%)[11]. In 1999 alone, the top three causes of fires were electrical distribution equipment (21.4%), open flame, ember or torch (21.4%), and intentional (14.3%) [11]. An important category of fires that NFPA does not discuss explicitly is the occurrence of fires during renovation. Renovation operations are behind the fires caused by open flame, ember or torch fall, as well as many electrical and arson related fires [12].

There is no statistical data available that examines how fire retardant treated plastics will alter expected rates of fire in museum; however, it is expected that flame retardants make materials harder to ignite, and slower to burn with reduced heat release rates. This is meant to limit the total quantity of material that will be involved in a fire, potentially stopping the spread of fire

It is the job of the fire protection engineer to consider the consequences of fire where others may not. Looking at the process of a fire, many museums rely on passive fire protection, such as the use of fire walls or barriers and fire retardant materials, paired with active fire protection, such as fire alarms, detection systems and automatic sprinklers. All these factors selected to work together to mitigate the risk of fire, but it is important to also consider the bigger picture in a museum setting by looking at the new risks these fire protection systems may introduce.

Chapter 2 Literature Review

2.1 Risk & Conservation

The risk analysis posed by this thesis aims to find a balance between the risk of fire occurring in a museum or museum storage facility and the more long-term risk of possible contaminants entering the museum or museum storage facility environment due to agents that lessen the risk of fire. Fire and contaminants are two of the ten agents of deterioration listed by Waller in his article titled "Conservation Risk Assessment: A Strategy for Managing Resources for Preventative Conservation [1]." In this paper, the risk of contamination is divided into 3 separate types; 'type 1' is rare and catastrophic, 'type 2' is sporadic and severe, and 'type 3' is constant and gradual. Contamination due to the potential gases and vapors being emitted from the plastic sheeting used in storage or during renovation falls under the classification of 'Contaminants – Type 3,' because this type of contamination would indeed be fairly constant and gradual [1]. Fire is considered to be type 1 only, since fires occur rarely, but when they do occur, they are generally catastrophic [1]. The risk of fire is dependent on many other factors, such as the presence of automatic fire suppression systems, ignition sources, oxidizers, etc.

A risk management approach applied to preventive conservation specifies four steps that are followed in almost all risk assessments:

1) identify all risks to collections,
2) assess the magnitude of each risk,
3) identify possible mitigation strategies, and
4) evaluate the costs and benefits associated with each strategy [13].

These steps are fairly straightforward; however, when the mitigation strategy becomes a risk, the approach tends to get more complicated. This rating system serves to

identify the risks to museum collections, and the magnitude of each risk is the product of the probability and severity, which have been dealt with by the 'type'-ratings for each risk.

In order to identify possible mitigation strategies, Waller suggest three basic means of control for mitigating a risk:

1) eliminate the source of the risk,
2) establish a barrier, and
3) act on the agent responsible for the risk [13].

These approaches can become more complicated in the case of flame retardant plastics. For instance, leaking water (on of the ten agents of deterioration) is a risk which is mitigated by the use of plastic covers as an established barrier in storage. The presence of plastics in storage increases the fuel load and overall risk for the spread of fire, if fire does occur. In order to reduce the risk of fire in the presence of extra fuel load, flame retardant plastics are used. The flame retardant plastics used to mitigate risk of fire introduce possible contaminants, and the mitigating strategy to protect against contaminants would be to eliminate the source of risk, or by removing the fire retardant plastics. A conflict in the strategy exists and so the solution is to determine which mitigation strategy has more benefits than costs. Perhaps assessing the magnitude of each risk prior to determining mitigation strategies will clarify which risks are great enough to call for mitigation approaches.

Within the three means of control, there are eight sub-levels which Waller lists: location, site, building, room, cabinet, specimen, policy and procedure [13]. Each facet can be evaluated for potential ways to reduce risk. However, the aim of this thesis is far

more specific, i.e., to look at the use of plastic sheeting, so that this level of specificity and control are not considered in this study.

In assessing the costs and benefits associated with the proposed mitigation strategies, it is noted that one strategy to reduce the risk from one agent of deterioration will influence the risk from another agent [13]. Another assessment point includes the costs and benefits associated with both implementation and maintenance stages. Finally, an evaluation of the effect of a proposed strategy on risks other than those to collections must be considered. Health and safety of the staff, visitors and users of a collection can be affected by certain mitigation strategies, even if the collections will benefit from them [13].

In his most recent study on preventive conservation planning for large and diverse collections, Waller explains that magnitudes of risk over a one hundred-year forecast period can be estimated using models to evaluate *Fraction Susceptible* (FS), *Loss in Value* (LV), *Probability* (P) and *Extent* (E) for each risk [14]. FS is the portion of a collection that is potentially subject to loss or damage by exposure to the risk being considered. LV is defined as the maximum reduction in value resulting from exposure of the FS to the risk in question. The P is defined as 1 for type 2 and type 3 risks because these risks are certain to occur, and evaluated for type 1 risks as necessary. The E is the extent to which a risk is expected to produce the LV to the FS over a specified period of time [14].

The following equation can be used to then calculate the magnitude of risk for each identified risk.

$$MR = FS \times LV \times P \times E$$

Equation 2.1-1. Magnitude of risk [14].

Waller asserts that the data required for estimating magnitudes of risk is becoming increasingly available, but for those that cannot be estimated reliably, the following possibilities are suggested.

1) The risk cannot be quantified accurately but it is known to be so high that it must be accorded a high priority for mitigation.
2) The risk cannot be quantified accurately but is known to be so low that it can be ignored
3) The cost of mitigating the risk to a known, low level is less than the cost of research or consultation needed to determine the magnitude of the risk accurately.
4) External consultation or new research is required to establish the magnitude of the risk [14].

The study also suggests that individual objects within collections be categorized by their value to the institution. These categories generally range from items that are literally priceless because they are one of a kind, to "working materials" that are worth very little [14]. Using this rating system, it is often possible to split up a collection and focus more attention on the more valuable objects. Although it may seem unwise to consider parts of a collection, this approach can be more cost-effective in the long run.

In the 1999 National Conference on Cultural Property Protection Proceedings, a risk-based approach to fire protection in museums that weighs the various alternatives and levels of protection against the cost and potential risk is presented [12]. The study has an excellent discussion of a fire-specific approach to risk assessments in museums. The paper applies a direct approach to risk management by discussing new technologies available to museums and how they fared in situ. The study has a pragmatic approach to determining relative values of objects, including considerations ranging from cultural significance to political value. The study also suggests rating the potential severity of a

fire once it has been started, using such factors as the construction of the structure, fire walls, combustibles present, and detection and suppression systems present.

2.2 Corrosion Testing in Museums

The Oddy test is a procedure followed in museums to determine if materials to be used in the display of artifacts will contribute to their degradation by means of chemical damage [15]. Small metal foil coupons, generally lead, silver or copper, are used as canaries in the test, allowing for a simple yet controlled way to create an environment in which the metals are exposed to each display material in question [15]. An accelerated aging process is performed over the course of four weeks, and the metal coupon samples are visually rated for the occurrence and amount of corrosion. The rating of corrosion is fairly subjective due to the nature of the visual assessment; however, it allows for comparison between exposures to different materials. Measures have since been taken to try to standardize and improve the test, though the basic idea remains the same [8, 9].

In response to Oddy's test, other conservation scientists have designed more rapid small scale tests to look at corrosion caused by display and storage materials on specific metals. In 1982, Daniels and Ward designed a rapid test for the detection of substances that will tarnish silver [16]. The idea behind the methodology is that a sodium azide based solution decomposes when in contact with materials which can tarnish silver by evolving hydrogen sulphide. The test can assess the potential severity of the material to tarnish silver under a microscope in a matter of minutes[16]. In 1990, Berndt discussed a method for testing corrosivity of atmospheres containing organic acids, which usually means environments with wood products in museums. [17].

At the Saving the Twentieth Century symposium held in Ottawa, Canada in 1991, Green and Thickett presented their research on modern metals in museum collections. Silver, copper and lead are the usual metals tested in an Oddy test because they are the common metals found in historic artifacts and are susceptible to corrosion. The research conducted was intended to adapt the Oddy test method to fit metals found in modern artifacts, such as aluminum, zinc and magnesium. It was found that the Oddy setup could be used to predict corrosion in these metals. However, it was also concluded that similar results could be found using the original Oddy test metals, and so if care were taken in selecting display and storage materials, the original test method would be acceptable [18].

Zhang et al. discuss the iodide-iodate test for volatile organic acids and the chromotropic acid test for formaldehyde, along with their uses for determining the presence of damaging volatiles in the materials selected for storage and display of museum objects [19]. Although these tests, when performed together, are good at predicting the safety of a material that may contain organic acids or formaldehyde, this research still concluded that the Oddy test would provide more information regarding other corrosive gases, and that Oddy's test is the most informative if time permits [19].

In 1995 Green and Thickett wrote another article further discussing the Oddy test and revising its methodology [20]. The study examines Oddy's test and seeks to eliminate any uncertain variables in the testing procedure. Statistical analysis was performed for results from first and second comparisons of the coupons following the test. The purpose of the paper was an attempt to standardize the Oddy test method, which continues to be adapted by individuals performing the tests according to available testing supplies [20]. In 1999, Bamberger, Howe and Wheeler developed a "three-in-one Oddy

test" where all three metals being tested (silver, copper and lead) were tested at the same time[8].

2.3 Electrochemical Testing

Electrochemical testing as an alternative method for assessing the effects of exhibit materials on metal artifacts was suggested in a paper published in 1998 in the journal Studies in Conservation by Reedy, Corbett and Burke [10]. In their paper, a new methodology measuring polarization resistance is used to rapidly and objectively identify display and storage materials that may cause damage to museum objects. The results of the new test method are shown to compare to the Oddy test, and to provide quantitative calculations of corrosion in milli-inches per year for a specific metal in the presence the extract solution of a particular material [10].

Standardized corrosion tests using electrochemical methods have been used mainly for industrial applications. Exposure to volatile, corrosion-causing contaminants is a recognized threat in industry and tests similar to the Oddy test were developed to address the problem. The tests used in industry generally rate the development of corrosion by quantitatively measuring change in weight of the metal coupons rather than of rely on visual assessments [10].

Corrosion scientists recognize that "when corrosion occurs, the current that flows between individual small anodes and cathodes on the metal surface causes the electrode potential of the system to change [21]." In Siebert's 1985 paper a method for indirectly evaluating the resulting current on a metal specimen is explained [21]. At the time of Siebert's paper, electrochemical methods generally used in industry were electrical

resistance, Tafel extrapolation, linear polarization and potentiodynamic polarization, and each method is described in his paper.

In Berke and Hicks' paper, methods for measuring a rate of metal loss due to corrosion are discussed [22]. The paper essentially examines the two main methods used for measuring corrosion: polarization resistance and electrochemical impedance spectroscopy (EIS). Polarization resistance acts to quantify "…the degree to which the system resists corrosive attack by the environment [22]." This paper references the ASTM G59-97 Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements, which describes the procedure used to determine corrosion potentials [23]. The test method uses a potentiostat "…to displace the equilibrium of the metal by about 10 to 20 mV as measured relative a reference electrode, and the current flowing between the metal and a counter electrode is measured [22]." The method described here for measuring corrosion on steel rebar in concrete is the same basic procedure being applied by Reedy et al. for museum applications [10].

There are a few other ASTM standards dealing directly with electrochemical tests. ASTM G3-89 Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing deals with the reporting and displaying of electrochemical corrosion data [24]. Although it does not include any testing methodology, it explains how to compile the results of any testing so the collected data can be compared to other standardized reports of similar data. ASTM G5-94 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements describes the procedures for checking experimental technique and instrumentation to ensure that the tests performed are repeatable [25]. Finally,

ASTM G102-89 Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements explains how to convert the results of the electrochemical measurements and polarization resistance values to rates of uniform corrosion [26]. The standardized practices provided in these reports are important in the analysis of the data because they allow for direct comparison between different materials. It will be important for the conservation related corrosion tests to adopt a similar standardized procedure if electrochemical testing replaces the Oddy test.

According to Reedy et al., "electrochemical tests are intended to simulate the corrosion behavior of a metal under the influence of a specific environment [10]." To simulate the environment formed by a potentially corrosive solid material, aqueous extractions from the display and storage materials to be tested were used. These extractions were prepared according to a modification of the ASTM C871-95 Standard Test Method for Chemical Analysis of Thermal Insulation of Materials for Leachable Chloride, Fluoride, Silicate and Sodium Ions [27]. The standard describes how to extract water-leachable ions in insulation materials, but has been extended for any material to be tested for use in display or storage. For this thesis, a modified version of the standard procedure will be used to make aqueous extractions from the plastics being tested.

2.4 Flame Retardants

Flame retardants have been used as additives to polymers, although the way in which these chemical additives work was not fully understood until more recently. Lindemann's 1969 journal article summarizes the current use and understanding of flame retardants in plastics [28]. The additives used at the time were said to have "a certain type of instability," which was thought to be responsible for the flame retarding

properties, but was also was known to be the cause of "general degradation of the plastic system from both physical and chemical forces[28]." The paper outlines halogenated and phosphorus based compounds that were used at the time, as well as ethers, acid derivatives, polymeric compounds, miscellaneous compounds, and free radical synergists.

In 1973, J.W. Hastie published a paper discussing the molecular basis of flame inhibition that discussed the role played by inorganic chemical additives in fire retardancy and flame inhibition [29]. This paper was one of the earliest papers published that discussed the chemistry of the gas-phase mode of flame retarding mechanisms at a molecular level. The paper was reprinted in 2001 because it is considered to be something of a seminal work.

In 1984, the Fire Retardant Chemicals Association published a document compiling articles concerning the flame retardancy advances in fire safety. The document discusses the roles of bromine-containing organic compounds that are used as flame retardants and outlines the criteria used to select the flame retardants for different materials and purposes. It also discusses how the additives will affect the product in terms of processability and properties. A section on the fire retarding of polyolefins reveals that chlorinated agents used to be employed as the halogen for fire retarding, but that "bromine containing products with greater stability [have] been developed [30]." The amounts of chlorine required to make polyolefins flame retardant were extremely high, but less bromine product can be used with a small amount of antimony trioxide to achieve the same level of protection.

In his 1992 paper, Babrauskas looks at real fire performance in fire retardant treated plastics rather than relying on the various standard benchmark tests [31]. The study examines whether the use of flame retardant treated plastics will reduce the overall fire hazard when compared to similar non-flame retardant items. In these experiments, a Cone Calorimeter was used to determine the heat release rates, as well as the different chemical components found in the products of combustion, such as CO, CO_2, HCl, HBr and HCN. Real-scale tests were also run and the relative fire hazard was quantified according to the time necessary to reach untenable conditions in the burn room or in a target room adjacent to the burn room. This was done by looking at smoke and CO yields. The hazard findings are shown below.

- "The average available escape time was more than 15-fold greater for the FR products in the room burn tests.
- The amount of material consumed in tests of the FR products was less than half the loss in the non-fire retardant (NFR) tests.
- FR products, on the average, gave ¼ the heat release of NFR products.
- The production of CO for the FR tests was about half of that for the NFR ones.
- The production of smoke was not significantly different in room fire tests between FR and NFR products [31]."

In conclusion, the study "demonstrated that if sufficiently effective FR agents are used, any effects of increased yields of smoke or CO are more than compensated by the decreased burning rates [31]." It also suggested that if the results of bench-scale tests could be better interpreted, they would be able to answer most questions about FR materials rather than the costly endeavor of a full-scale test.

In the book Fire Retardant Materials, there are a number of chapters dealing with polymers and flame retardants [32-35]. The introduction describes polymer combustion, condensed phase pyrolysis and smoke formation [34]. The next chapter discusses the

current understanding of mechanisms and modes of action in the flame retardancy of polymers [33]. The text by Purser also includes a discussion of toxicity of the fire retardant chemicals and a discussion by Georlette of the applications of halogen flame retardants [32, 35]. In their book, Lomakin and Zaikov discuss recent knowledge about flame retardants in polymers, including lists of the chemical structures and manufacturers, toxicology, and ecology [7]. These two books provide an explanation for the chemistry behind fire retardants, and both give a comprehensive picture of the action of a number of different types of flame retardant additives.

In 2003, a market report regarding Flame Retardants for Plastics was published [5]. The report lists all the flame retardant additives currently being used in industry and also identifies their potential markets. The report also delves into fire testing and environmental and regulatory matters, which have become more prevalent in recent times. In that vein, there has been recent attention to the apparent environmental dangers associated with brominated fire retardants.

2.5 Environmental Issues & Toxicity

Due to unforeseen human and environmental impacts, there are a growing number of stringent limitations on brominated flame retardant materials. As already discussed, the pressure to determine if BFRs are a hazard to the environment, wildlife, and humans is mounting. While Europe is taking action against many BFRs, the number of BFRs being manufactured for industrial and commercial uses continues to climb. In the past few decades, much work has been done in the attempt to determine if brominated fire retardants are a greater hazard to life and the environment than the fires they are meant to prevent. The industries that produce these chemicals are eager to point out the benefits

provided by the fire retardants in terms of lives and dollars saved from destruction or damage in fires. However, as early as 1979, the presence of BFRs have been detected in the environment "in soil and sludge samples collected from areas surrounding polybrominated diphenyl ether (PBDE) manufacturing facilities in the US [36]." From this time forward, a number of studies have looked at how the fire retardant chemicals have infiltrated the environment and our bodies.

The Bromine Science and Environmental Forum (BSEF) printed an introduction to brominated flame retardants in 2000, which reports that bromine based fire retardants are the largest market for fire retardants [37]. Aside from the marketing and uses of these chemicals, the report addresses health and environmental issues associated with brominated fire retardants. The report explains that although Octa-brominated diphenyl ethers (Octa-BDE) and Deca-BDE are not bio-accumulative, Penta-BDE has been found in the environment, and traces of Penta- and Tetra-BDE have been found in human breast milk. Polybrominated biphenyls (PBB) were identified to have potential endocrine disrupting chemicals, and production of these chemicals was ceased in May 2000. Other brominated fire retardants are considered to have either little potential for bio-accumulation or to be relatively harmless, although some can be found in humans [37].

In an article published in 2000, Tullo discusses the evolution of plastics additives [38]. A major point in the paper is the growing use of brominated flame retardants in industry (approximately 5% per year) despite the signs that these chemicals may be dangerous [38]. However, testing still points to the safety of many of the brominated chemicals, and the threat of fire in a world increasingly filled with plastics requires some kind of flame retardant. According to the article, the search for fire retardants that are not

halogenated continues; when phosphorus-based agents can be used, they are preferred, but the brominated flame retardant market still continues to grow.

According to a paper published in 2002 by de Wit, the PBDE levels found in sediment and biota in Europe, Japan and North America seem to be steadily increasing [39]. This increase is likely to be detrimental to wildlife, children, indigenous peoples and fish eaters. Because the knowledge about these chemicals is limited, specifically in terms of their sources, environmental behaviors and toxicity, the article asserts that it is difficult to accurately assess the full risk involved with the continued use of these chemicals.

In 2003, a press release from the European Brominated Flame Retardant Industry Panel (EBFRIP) reported that the levels of bromine in plastics as flame retardants did not adversely affect energy recovery equipment for household water treatment. The study showed that when various plastic products (some containing BFRs) are being recycled, the equipment used to break them down was unaffected by corrosion as long as the total amount of BFR treated plastic did not exceed 3% of the total weight of materials being recycled [40]. The report contains a chapter discussing the possible effects of bromine containing compounds and how they might be corrosive to metals [41]. According to the report, there is not much literature available dealing only with the corrosivity of bromine and its derivatives; however, some data is presented regarding corrosion rates of several alloys in bromine at elevated temperatures [41]. The study found that corrosion in the waste to energy (WTE) plants is generally caused by high chlorine levels in the waste rather than by bromine, but suggested that more research needs to be done that specifically examines the effects of bromine. The study indicates that at the elevated

temperatures needed for the recycling process, bromines are released and can be damaging, but nothing is mentioned regarding the treated materials at normal ambient temperatures.

In his 2003 paper, Darnerud looks at each of the BFRs and compiles are the critical harmful effects of each [42]. He begins with the PBDEs, looking at each of the three most commercially used congeners: PentaBDE, OctaBDE and DecaBDE.

The critical effects of PeBDA are noted to be developmental neurotoxicity and altered thyroid hormone homeostasis at higher doses [42]. The lowest observed adverse effect level (LOAEL) for PeBDE was found to be 0.6 – 0.8 mg/kg body weight in neonatal mice, so it is difficult to say how this can be compared in humans [42]. For OBDEs, morphological effects were seen in the livers of adult rats dosed with dietary OBDE at 10 mg/kg body weight [42]. Other adverse effects included problems with thyroid glands, kidneys, the haemological system, and signs of fetal toxicity in rabbits and rats[42]. DBDE was found to be the least toxic of the PBDEs, with a LOAEL of 80 mg/kg body weight at which point thyroid hyperplasia, liver enlargement and hyaline degeneration in kidneys occurred [42]. The DBDE study also included a carcinogenicity study, which showed the formation of adenomas and carcinomas at doses of 1200 mg/kg body weight per day and higher [42].

The same study looked at tetrabromobisphenol A (TBBPA) and found that in the mammalian studies, only doses in gram/kg body weight were effective yielding a low toxicity rating, while other studies found that lower doses could cause slight renal impairment in rats [42]. Hexabromocyclododecane (HBCD) has been studied as well, and it has been shown that although more studies need to be conducted, in rats, the

LOAEL of 100 mg/kg body weight per day was found to cause increased liver weight[42]. Polybrominated biphenyls (PBBs) have been found to cause reproductive effects and carcinogenic effects at the lowest administered doses in animal studies. This chemical is perhaps the most dangerous, which is why it is no longer used.

In 2004, D'Silva et al. authored an article, which studies the increasing concerns with flame retardants. The paper covers current knowledge relating to the issue, including how BFRs are useful in slowing the spread of fire and preventing loss of life and property, how they work and how they affect the environment. The goal of the study was to look at other BFRs that have since been banned as persistent organic pollutants (POPs), and to use the methods for determining their negative characteristics to closely follow newly emerging POP characteristics in the BFRs currently being manufactured [43].

A short article by Hites in the Journal of Environmental Monitoring from 2005 tracks various types of BFRs and where they have been found in the environment. This particular article explains that it is the non-reactive (additive), non-polar BFRs which are generally found in the environment and reviews some of the problems that have occurred because of these chemicals [44].

Aside from the dangers from the very presence of some of the BFR chemicals in the general environment, there is also concern about the formation of toxic products and their rate of evolution during fires. The production of both acid gases and carbon monoxide need to be considered because the toxic yields from materials treated with FR chemicals might be greater than those from untreated materials. In other words, the

chemicals that are meant to protect from fire might actually contribute to an increased toxic environment during a fire, depending on the situation. According to Purser,

> "In terms of toxic risk from fires, the cost/benefit relationship for fire retardant use therefore depends upon how many fires and their subsequent hazards are prevented by the use of the FR-material and the extents of the toxic hazards from the remaining fires occurring that involve FR-materials. The toxicity of fire retarded materials therefore becomes an issue when the toxic hazards (both direct and environmental) from fires involving fire-retarded materials becomes significantly greater than those from fires involving equivalent non-FR materials. The toxicity of FR materials becomes a more serious issue when the toxic risk arising from the use of a fire retardant becomes greater than that when the fire retardant is not used [35]."

This same argument may be applied to the use of treated and untreated plastics in the museum environment. Although life safety is not the main focus of this thesis, it is also very important, and the approach to life safety directly correlates to safety of the museum objects. There is a set of certain "toxic" contributors to metals and other museum objects, fire being one of them, and corrosive chemicals being the other. Just as in the case of toxic hazards to humans, a balance must be found.

After performing a review of the literature concerning risk and conservation in museums, corrosion test methods used in museums and in industry, and fire retardant chemicals, a compelling question arises regarding whether or not fire retardant treated materials have a place in museums and libraries or archives. There has been little attention from the museum world to the chemical additives used for fire retarding the plastics that may be used in both display and storage, and how these chemicals might be affecting museum objects.

In terms of risk assessment, Waller's model provides a good framework for assessing risks in museums, and can be manipulated to focus specifically on the question

of flame retardant plastics. The most difficult aspect of the risk assessment will be assigning probabilities to each risk. Research on the occurrence of fires in museums, and data about the effects of the plastics both thermally and non-thermally, will allow reasonable rating of these mitigating strategies.

In the museum world, chemically unstable materials are avoided if possible. Considering the increasing incidence of brominated fire retardants (BFRs) in the environment, it seems that the BFRs that are used in flame retardant plastics are leaching out of their substrates and into surrounding environment by some mechanism. This bodes poorly for FR-treated plastics in terms of museum-worthiness. However, it is important to also consider the threat of fire in a museum or museum storage area, and the potential property losses that could be suffered. The levels of BFRs needed to treat a plastic are lower than the levels needed for the more corrosive chlorinated fire retardants, so it may be that the overall levels of BFRs in the plastics used for museum purposes are harmless in the carefully monitored environments of a museum.

Although this study's focus is fire retardant-treated plastic sheets polyethylene sheeting, it will serve a more general purpose to the museum world. The knowledge of how fire retardant chemicals in these plastics may affect museum objects, and the process by which this knowledge may be achieved can be extrapolated to many other situations. Flame retardant chemicals are increasingly common additives in many materials, and sometimes collection objects themselves have been treated with fire retardants to assist in their preservation. However, a final answer about the usefulness of FR plastics in museums will be best decided on a case-by-case basis. This study provides an outline on how to approach this decision.

Chapter 3 Plastics & Flame Retardants

3.1 Plastic Sheeting in Museums

3.1.1 Polyethylene and Its Use

The main focus of this research is polyethylene thermoplastic sheeting. When thermoplastics undergo deformation at elevated temperatures, the deformation is reversible, while thermosetting plastics undergo irreversible changes when heated. Because this study examines museum applications of plastic sheeting, the main polymer that will be studied is polyethylene. At present, the Smithsonian Institution almost exclusively uses pure polyethylene plastic sheeting in storage where applicable, because it is considered to be one of the most chemically neutral and stable materials available for this purpose [3].

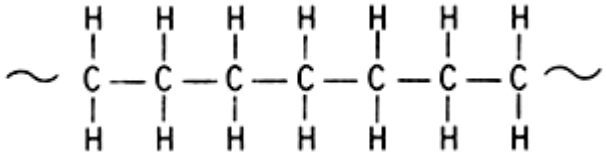


Figure 3.1-1. Polyethylene molecular chain structure.

Polyethylene is one of the most familiar and simplistic polymers, shown in Figure 3.1-1. Its molecular chains associate through weak van der Waals forces, or non-covalent forces. Polyethylene is inexpensive and has good chemical resistance. Although it is safe by museum and food standards, it is prone to photodegradation from ultraviolet (UV) light depending on its manufacture. The plastics do best in normal room temperatures, but are easily ignitable and highly flammable in the presence of elevated temperatures, shown in Table 3.1-1, or small ignition sources.

Polyethylene is felt to be well suited for use in museum environments for the protection of collections, and museum environments are generally well suited for the preservation of polyethylene, since little UV light is expected to reach the plastics. The museum environment is normally stable in terms of temperature and relative humidity. Polyethylene sheeting is ideal for blocking dust and moisture from reaching objects. "Polyethylene film is frequently used as an isolating barrier" in museum storage and display due to its effectiveness in blocking water, oxygen and carbon dioxide [3].

3.1.2 Combustion of Polyethylene

Primarily because of its linear chain structure, polyethylene will soften or melt and start to flow at relatively low temperatures. Additional heat will cause it to decompose or pyrolyse, and to evolve smaller, volatile molecular species [34]. Some of the thermal properties of low density polyethylene are shown in Table 3.1-1.

Table 3.1-1. Properties of low density polyethylene (LDPE) [34].

Glass Transition	< 0 °C
Melting Temperature	100 – 120 °C
Decomposition Range	340 – 440 °C
Flash Ignition Temperature	340 °C
Autoignition Temperature	350 °C
Heat of Combustion ΔH_c	46.5 kJ/kg

During small-scale mock artifact burn tests, as shown in Figure 3.1-2, when polyethylene is draped over a mock artifact as a barrier it burns readily. A flaming drip, which could cause fire spread and damage to surrounding objects, is visible in this image at the bottom left. There was very little smoke, and there was no residual char as the

entire sheet was consumed, except for a few drips that landed in locations where there was not enough thermal feedback to continue the combustion process.

Figure 3.1-2. Mock artifact burn test for pure polyethylene plastic sheet with flaming drip.

When a polymer is exposed to sufficient heat, it will begin to decompose or pyrolyse, allowing the decomposition products to mix with air. For polyethylene, the decomposition range is between 340 – 440 ºC, as shown in Table 3.1-1. If the temperature is high enough, and there is enough oxygen present to mix with the flammable volatiles, then the plastic will ignite. For polyethylene, autoignition will occur at 350 ºC and flash ignition will occur at 340 ºC – fairly low temperatures compared to other common thermoplastic polymers. Self-sustaining combustion cycles are achieved when sufficient heat is evolved by the ignited flame to keep the decomposition rate of the polymer high enough to maintain a steady concentration of the vapor fuel within the flammability limits of the material [34]. Figure 3.1-3 shows the various steps involved in

polymer combustion. The term "thermal feedback" indicates an external heat source such as radiative heat or a flame.

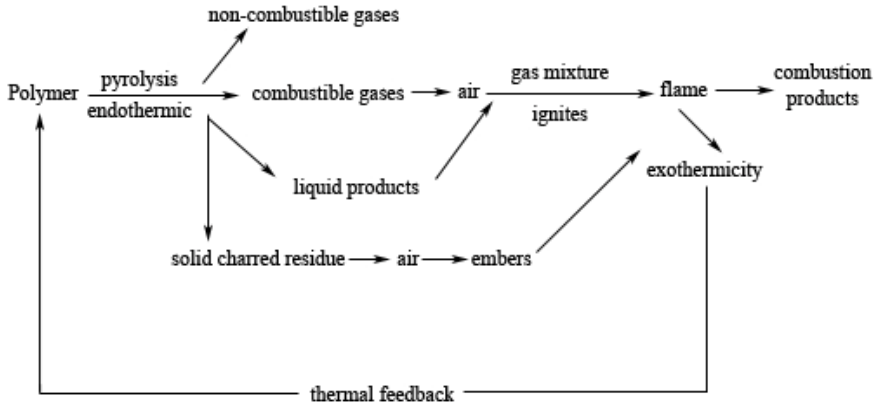


Figure 3.1-3. Schematic of the processes involved in polymer combustion [34].

Heat of combustion is the energy released as heat when a compound undergoes complete combustion with oxygen. The heat of combustion for low density polyethylene is 46.5 kJ/kg, a value higher than other common thermoplastic polymers. This means that not only does it decompose and ignite at lower temperatures, but it releases more heat per unit mass as it undergoes combustion. The polyethylene sheets used are thin, generally between 2 and 14 milli-inches (mil), so even big sheets do not provide a huge amount of fuel per unit area and burn away fairly quickly. The plastic sheets do extends over large spaces and this means that once ignited, the fire can spread rapidly along the plastics. It is also likely that large spools of extra plastic would be present in storage areas; these are a more densely packed fuel source. Polyethylene, though safe for normal museum environments, is a likely source of fuel in a fire, and has the potential to easily spread flames and heat.

3.2 Flame Retardant in Plastics

3.2.1 History of Flame Retardants

The purpose of flame retardants is to "slow down the initial burn rate and thereby […] help increase the time to flash-over, giving the occupant more time to escape [37]." Much was known about using chemical mechanisms to reduce flammability since ancient times. Flame retardant chemicals can be inorganic, organic, mineral, halogen-containing or phosphorous containing. Even if earlier civilizations did not understand the physics and chemistry taking place, they figured out ways to create fire retardants [7]. Some early historical developments in flame retarding are shown in Table 3.2-1.

Table 3.2-1. Early historical fire retardant developments [7].

Development	Date
Alum is used to reduce flammability of wood by Egyptians	About 450 BC
The Romans use a mixture of alum and vinegar on wood	About 200 BC
Mixture of clay and gypsum used to reduce flammability of theater curtains	1638
Mixture of alum, ferrous sulfate and borax used on wood and textiles by Wyld in Britain	1735
Alum used to reduce flammability of balloons	1783
Gay-Lussac reported a mixture of $(NH_4)_3PO_4$, NH_4Cl and borax to be effective on linen and hemp	1821
Perkin described a flame-retardant treatment for cotton using a mixture of sodium stannate and ammonium sulfate	1912

The early twentieth century brought with it the arrival of synthetic polymers, which would begin to drastically change the materials used in everyday life, and from a

fire standpoint, would drastically change potential fuels. At the time of the invention of synthetic polymers, the fire retardants used were mostly water-soluble inorganic salts. These types of products were largely useless for the hydrophobic synthetic polymers, and so it was important to develop new fire retardants that would be compatible with the polymers [7].

The earliest of these polymer-compatible flame retardants was a treatment consisting of chlorinated paraffins and an insoluble metal oxide, with a binder resin. The insoluble metal was mainly composed of antimony oxide. This treatment was created for use in the Second World War to limit the flammability of canvas tents used by the military.

Over the past 40 years, the increased public demand for safety has spurred the development of more rigorous legislation regarding life safety in both public and private settings. As a result, special attention has been paid to fire protection, which, in turn, has created a surge of interest in the development of new and more effective fire retardant materials. Chemical treatments or additives are still being used for new synthetic polymers, but now it is also possible that the fire retardant or resistive element is incorporated into the chemical structure of the polymer. From 1960 – 1980 many of the current fire retarding materials that are used today were created, with a few notable exceptions as discussed below.

In the 1970s, the most common flame retardant polymers were thermosets such as unsaturated polyesters and epoxy resins. These thermosets included reactive halogen compounds and aluminum hydrate as additives to give them flame retardant properties. Phospate esters were also used as flame retardant additives in plasticized polyvinyl

chloride, cellulose acetate film, unsaturated polyesters and modified polyphenylene oxide [7]. The use of halogen-containing flame retardant additives was considerably less than the use of the aforementioned additives in the 1970s. These types of additives included the following:

- Dechlorane Plus – a chlorinated acyclic used for polyolefins
- Tris-(dibromoprpyl) phosphate
- Brominated Aromatics
- Pentabromochlorocyclohexane
- Hexabromocyclododecane – used for polystyrene

Although halogenated additives were not as popular at first, throughout the 1970s many new brominated additives entered the market, as well as a number of chlorinated products under the Dechlorane label. As the use of thermosets and thermoplastics became commonplace in large scale applications such as buildings, transportation, electrical engineering and electronics, and more rigorous safety legislation was introduced, new flame-retardant systems were developed. These systems consist of inorganic or organic compounds based on bromine, chlorine, phosphorus, nitrogen, boron, and metallic oxides and hydroxides. The specific formula of the system would be developed depending on the intended use of the final product.

Initially, polyethylenes were flame-retarded with chloroparaffins and antimony trioxide. However, a number of the chlorinated chemicals were shown to cause environmental problems, including polychlorinated biphenyls (PCBs), which were banned in 1970 due to high toxicity [5].

Currently, between 150 and 200 flame retardants have been designed to fit the requirements of the various markets they serve. The main chemical components used in these products are halogens (bromine and chlorine), phosphorus, inorganics and

melamine compounds. Figure 3.2-1 shows the percentages of each chemical component in the overall market of flame retardants. From this figure, it is evident that bromine based flame retardants dominate the market.

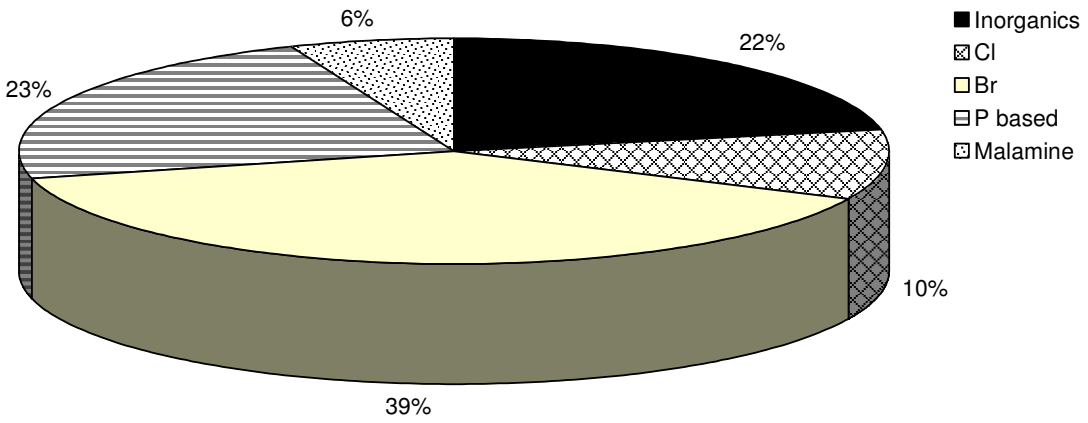


Figure 3.2-1. Major families of flame retardants and their prevalence in the FR market in 1997 [32].

3.2.2 Misconceptions

A serious problem with the so-called flame retardant plastics is that they are referred to as flame or fire retardant. This term may wrongly imply that the treated material is physically impervious to flame, and that it is effectively fireproof. In reality, flame retardant (FR) materials might be more suitably called "ignition resistant." While it is more difficult to ignite a FR treated material, once exposed to enough heat, a treated plastic will burn similar to a non-FR treated material. FR treated or not, in a full-blown fire scenario, all plastics will eventually become fuel.

3.2.3 Brominated Flame Retardants (BFRs)

The five major BFRs are tetrabromobisphenol A (TBBPA), hexabromocyclodocecane (HBCD), and three polybrominated diphenly ethers (PBDEs), all shown in Figure 3.2-2. Polybrominated biphenyls (PBB) are also shown in Figure

3.2-2 (A); however, these were removed from the market in the early 1970s because of toxic effects [6].

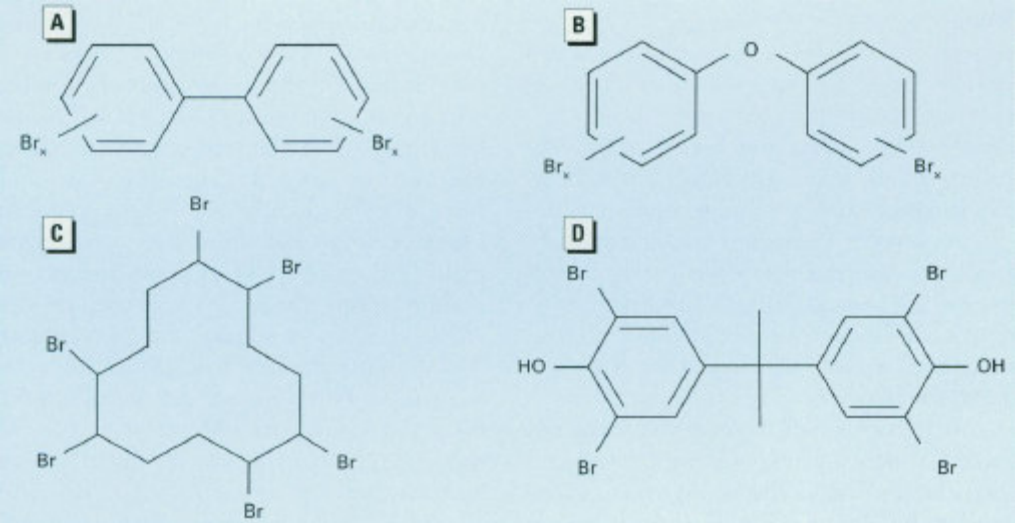


Figure 3.2-2. Chemical structures of (A) PBBs, (B) PBDEs, (C) HBCD and (D) TBBPA [6].

Brominated flame retardants are divided into reactives or additives. TBBPA and its derivatives are reactive BFRs, meaning that they are chemically bound to the polymer. The additive BFRs, including HBCD and the PBDEs, are simply added into the polymer mixture, but no chemical bonding occurs. Because of this, the additive chemicals are thought to be more easily released into the environment and have the potential to be more environmentally threatening [36].

There are a number of possible PBDEs, depending on the number of bromines present in the molecule; however, there are three major commercial types. These are Deca-BDE (DBDE), Octa-BDE (OBDE) and Penta-BDE (PeBDE) because they offer the most stability of the various congeners. According to the Bromine Science and Environmental Forum (BSEF), the polyethylene used to make films, foams, wires and cables is generally flame retarded with additive PBDEs, namely DBDE. Table 3.2-2 shows the volumes of each type of BFR used in 2001 by the region, and it is evident that

DBDEs are the most widely used of the PBDEs both in the USA and throughout the world [6].

Table 3.2-2. Major BFR volume (metric tons) estimates by region in 2001 [6].

BFR	Americas	Europe	Asia	Rest of World
TBBPA	18,000	11,600	89,400	600
HBCD	2,800	9,500	3,900	500
DBDE	24,500	7,600	23,000	1,050
OBDE	1,500	610	1,500	180
PeBDE	7,100	150	150	100
Total PBDEs	33,100	8,360	24,650	1,330
Total BFRs by region	53,900	29,460	117,950	2,430
% of total by region	26.5%	14.5%	57.9%	1.2%

PeBDEs and OBDEs are the least used presumably because they have been found to be harmful to the environment. Because of the findings against PeBDE, as of July 2003, the chemical was under voluntary ban in Europe; since July 1, 2006, a European Union directive has restricted the use of both PeBDE and OBDE in electrical and electronic equipment [6]. The state of California has also moved to ban the use of PeBDE and OBDE by 2008, and this has recently been approved as California state law [6].

According to their manufacturers, PBDEs very stable; however, there have been a number of studies that have found that "when PBDEs are dissolved in organic solvents, debromination occurs in the presence of UV light [6]." Larger PBDEs, such as DBDE, break down to lower brominated congeners, which are smaller and more easily infiltrate organisms, sediments and soils [6]. Therefore, PBDEs may be seen to pose a risk to normal and museum environments during their break down.

3.2.4 Antimony Trioxide

Antimony trioxide is added to most halogenated flame retardant plastics for a synergistic increase in the effectiveness of the chemicals. It cannot act as an effective fire retardant on its own. X-ray Fluorescence analysis of the various polyethylene sheets showed it was present in most cases. From a toxicological perspective, antimony trioxide is classified as group 2B by the International Agency for Research on Cancer (IARC), meaning it is "possibly carcinogenic in humans [45]." It is not expected to be active in the corrosion of metals.

3.2.5 Corrosivity of Bromine Containing Compounds

There is interest about what types of corrosive gases will be released if FR-treated plastic burn versus the gases produced by an un-treated polyethylene. Because of the potentially corrosive nature of the halogens and the specific museum setting, it is important to consider the corrosion at normal temperature conditions. It has been found that the polybrominated diphenyl ethers often debrominate, releasing bromine ions into the environment. These ions are very reactive with metals that are nearby, especially if there is moisture present, causing corrosion. It is known that that halogen species can also play an intermediate role in accelerating metal oxidation [41].

3.2.6 Flame Retardants: Advantages

Safety regulations are responsible for first specifying that flame retardant chemicals should be used in plastics to reduce flammability, thereby reducing loss of life and property from fire. In 1988 the United Kingdom passed legislation which required upholstered furniture to meet higher flammability standards, requiring that the fillings

and covers of most upholstered furniture be flame-retarded [46]. In the United Kingdom alone, government scientists have estimated that more than 3000 lives were saved in the period between1988 – 2000 as a result of FRs [46].

According to the Bromine Science and Environmental Forum (BSEF), there were more than 4,000 fire deaths in the US alone in the year 2000 and of these, the study estimates that 280 could have been avoided by the use of FRs [46]. BSEF also reports that in Europe, the EU Commission has estimated that there has been a 20% reduction of fire deaths as a result of the use of flame retardants in recent years.

BSEF compares the fuel load of a non-FR television set to 6 liters of gasoline. Similarly in the case of televisions, the introduction of a higher fire safety standard in the US for television enclosures has led to a 73% decrease in the incidence of fires involving televisions. In Europe there is no comparable regulations and the number of fires involving televisions, with resultant deaths and injuries, have continued to climb [46].

"Overestimating risks from FRs might result in a net adverse effect on public health if the uses of FRs that could reduce the risks of death and injury from fires were avoided because of minor toxicological risks estimated through such conservative assumptions [47]." With the overwhelming number of studies performed showing the potential environmental dangers associated with the use of the BFRs and other FR chemicals, it is important to recall the reason why these chemicals came into being in the first place. Their effectiveness at reducing the number of deaths from fire, and reducing the number of fires overall should not be overlooked.

According to a study performed by Babrauskas [31] in many various polymers, both flame retardant (FR) and non-flame retardant (NFR), were subjected to different fire

performance tests, a few conclusions may be drawn regarding FR polymer materials. It was determined that different FR treated polyurethane foams, when exposed to low irradiance levels (25 kW/m^2), performed much better than NFR polyurethane foams with regard to time to ignition. As the irradiance levels were increased, this effect on ignition time became small. Overall, it was found that "…the resistance to small ignition sources is noticeably improved, while actual fire performance, once ignited, is not much changed [31]." The flame retardant polymers tested were bromine-treated polyurethane foam and a phosphorus and chlorine treated polyurethane foam, which were compared to untreated PU foams. In low irradiance tests, the bromine FR was more effective than the chlorine and phosphorus FR in terms of ignition time, but as the irradiance was increased, the two performed very similarly.

In terms of real-scale fire hazards, Babrauskas' tests concluded that the amount of material consumed in tests of the FR products was less than half the loss in the NFR tests [31]. It was also found that the FR products gave ¼ the heat release of NFR products on average. The production of CO for the FR tests was about half of that for the NFR tests. However, the materials used in these tests also included TV cabinets, chairs, and cables, and as a result, the results do not specifically apply to pure plastics.

As far as the overall life-safety benefits from using brominated flame retardants (BFRs), estimations have been made of the number of lives saved by brominated flame retardants annually in the USA. Four products containing BRFs were analyzed; television and appliances, electrical wiring, fabric back-coating and cushioning. The studies estimate that somewhere between 630 and 1000 lives are saved per year [5]. How this particular statistic relates to the usefulness of fire retardant plastics in museums is

complex. Perhaps the BFRs allowed for longer escape time for occupants but did not change the overall fire size which would still destroy property. It is interesting to note that it is nearly impossible to predict the number of prevented ignitions due to BFRs, a statistic that would be extremely useful in determining the usefulness of flame retardants in a variety of applications.

Chapter 4 Analysis of Corrosion of Metal Materials in Museums

4.1 Corrosion

The corrosion studied here is that which occurs at the interface between metal and an electrolyte solution by means of electrochemical reactions. Although electrochemical-based corrosion readily takes place on most metals that are submerged in aqueous solutions, it is possible to a similar type of have corrosion develop in gaseous environments when a thin film of moisture forms on the metal surface and acts as an electrolyte [48]. The rate of corrosion at a metal surface can be determined by finding the equilibrium between the opposing chemical reactions that make up the effective electrochemical cell. These reactions are comprised of anodic and cathodic reactions.

The anodic reaction oxidizes the metal, dissolving ions and generating electrons into the metal. The anode is the electrode through which positive electric current flows into a polarized device, while the cathode is the electrode through which positive current flows out of that device. The cathodic reaction, in which the electrolyte species is reduced, allows the oppositely charged ions of the reduced electrolyte species to bind to the electrons and form a new, stable compound. Oxidation of copper, for example, is shown in

Equation 4.1-1, and the reduction of bromine is shown in Equation 4.1-2. When the two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs [48].

$$Cu \rightarrow Cu^{+} + e^{-}$$
$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

Equation 4.1-1. Oxidation of copper.

$$Br_2 + 2e^{-} \rightarrow 2Br^{-}$$

Equation 4.1-2. Reduction of bromine.

Hypothetically, if the flame retardant molecules in plastics have undergone debromination, especially if the environment is moist, corrosion is expected to occur

since the liberated halogens act as oxidizing agents. When a metal such as copper comes into contact with an environment containing bromine, a redox reaction will potentially occur. The negatively charge bromide ions, Br^-, may also combine with positively charged Cu^+ and Cu^{2+} ions under various conditions, forming CuBr or $CuBr_2$. Many metals, such as Cu, will form an oxide layer on their surface in reaction to the atmosphere. If this layer inhibits further corrosion, then the metal is said to passivate [48]. However, the layer may breakdown in certain cases, which can result in small areas of corrosion, called pitting.

Solid- and gas-phase redox reactions are also theoretically possible, shown in Equation 4.1-3. Because CuBr and $CuBr_2$ are so soluble, they may not form in water, especially at low concentrations. If it is formed, hydrogen Bromide (HBr) may take part in a redox reaction with copper.

$$Cu + Br_2 \rightarrow CuBr_2$$

Equation 4.1-3. Solid- and gas-phase reaction between copper and bromine.

4.2 Corrosion Testing

4.2.1 Oddy Test

4.2.1.1 Uses of the Oddy Test

As previously mentioned, the Oddy test, originally devised by a conservation scientist named Andrew Oddy in 1973 for the British Museum, is intended to reduce the use of exhibit materials that could be corrosive or damaging to museum collections [15]. Oddy originally suggested that a piece of polished metal be placed in a glass jar with the exhibit material in question, and then the jar be placed in an oven at 60 °F for four weeks. This would essentially create a controlled environment where the polished metal,

representing a museum object, is exposed to volatiles from the exhibit material. The heating in the testing procedure accelerates the reactions. Because museum collections could be exposed to exhibit materials for long periods of time, it is important to try to create accelerated aging conditions. At the end of the month, the metal coupon is visually evaluated for corrosion, compared to a blank control test (no exhibit material included) and an unexposed polished reference coupon.

After the original Oddy test was published, many museums adopted their own version, and a uniform methodology has not been generally practiced. The three-in-one version of the test includes three metals, silver, copper and lead, in a single test jar, further simplifying the test method [8]. This test can be used to look at the potential effects any number of exhibit or storage materials, either solid or liquid, might have on metals. It is simple and cheap to perform, and uses materials already available in most labs, although it takes a month to get results.

Due to the subjective nature of the test, conservation scientists have been exploring ways to standardize and improve the Oddy test. At one point the addition of reference photographs for evaluating corrosion were added, rather than using reference coupons which could become discolored and corroded over time [18, 20]. Other efforts, like the addition of water, have been made to accelerate the evolution of potentially corrosive gases from the test material [20]. The test has survived because it is simple and inexpensive, and is better than relying on in situ observations after questionable materials have already been used in an exhibit. In addition, the test can be performed at almost any museum institution.

4.2.1.2 Problems with the Oddy Test

The Oddy test is limited in many ways: it is limited to the testing of metals, it takes a month to get results, and often the results are extremely hard to analyze. The Oddy test could potentially be extended to look at effects from exhibit materials on fabrics or paper products, but there are other tests that provide better, quicker results for these types of materials, such as the azide test, the iodide-iodate test, or the chromotrophic acid test. The biggest problem with the Oddy test is the subjective nature of the results. One study looked at statistical repeatability of the Oddy test between different laboratories and different raters of the coupons [20]. The study found that if a standard procedure was used within a laboratory on a small scale, the results obtained were in good agreement with each other; however, the results were not in perfect agreement across different laboratories [20].

The results of the Oddy test are reported in terms of the amount of corrosion incurred on the metal coupon. The severity of the corrosion is generally used to rate the tested materials according to their intended use for in display or storage. One system rates the tested materials as “permanent,” “temporary use,” “unsuitable,” or “?” for void results in terms of each type of metal [20]. Although this system gives an answer to whether a not a material seems safe for exhibit or storage purposes, it only gives qualitative results that are rated subjectively.

The Oddy test does not take very long to set up, but takes a month of waiting to get results. This is not always a realistic time constraint for museums that may need to know about exhibit materials within days or weeks. Exhibit materials can be changed at the last minute, or may not be available until shortly before construction begins. While

Oddy's test is simple enough for any lab or museum to perform, the problems involved may hinder the usefulness of the test, and ultimately, may hinder the validity of the results.

4.2.2 Electrochemical Testing

4.2.2.1 Electrochemical Corrosion Measurement

Electrochemical testing to determine corrosion on metals in specific environments has long been used for industrial purposes and is "widely considered to be a reliable approach to accelerated testing for assessing the possibility of corrosion under natural conditions, without changing the basic failure mechanisms involved [10]." Electrochemical testing methods can be used to rapidly measure very low corrosion rates, and are thus potentially useful to scientists in the field of conservation.

When a metal specimen is placed in an electrolyte solution with possible corrosive characteristics, the metal will assume a potential called the corrosion potential (or open circuit potential), E_{corr}. The current flowing between anodic and cathodic areas is measured and then used to calculate the rate of metal loss, or the rate of corrosion. Figure 4.2-1 shows a plot of the potential (E) versus the logarithm of absolute current. The curved lines show the cell current, which is he sum of anodic and cathodic currents (total current), measured as the potentiostat sweeps above and below the corrosion potential of the metal.

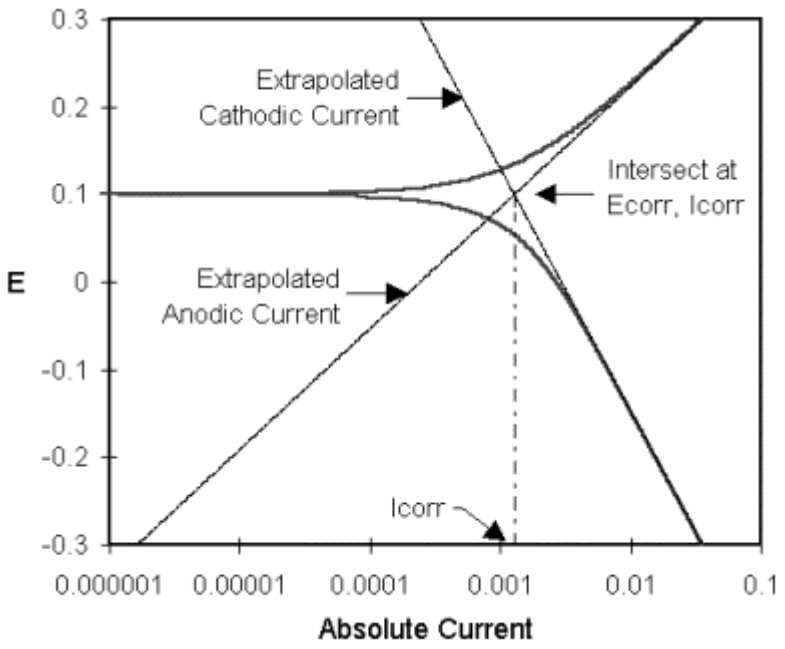


Figure 4.2-1. Corrosion process showing anodic and cathodic current components [48].

Before the input of applied voltage, the equilibrium potential assumed by the metal, or Open Circuit Potential (E_{oc}), is measured. The value of either the anodic or cathodic current at E_{oc} is called the Corrosion Current, I_{corr} [48]. If this value were easily measured, then it could be used to calculate the corrosion rate of the metal; however, it cannot be measured directly, and so it must be estimated using electrochemical techniques [48]. Controlled potential (potentiostatic) polarization allows for current to be measured. This means that the potential of a metal sample in solution is forced away from its Open Circuit Potential (E_{oc}), and the response, or current, of the metal sample is then measured. In looking at Figure 4.2-1, this is represented by moving either up (for an anodic region) or down (for a cathodic region) along the y-axis, which represents a change in the potential. If the potentiostat is used to force the potential to an anodic region, i.e., towards positive potentials from the E_{oc}, the rate of anodic reaction (corrosion) will increase and the rate of the cathodic reaction will decrease [48]. The

shift in potential will result in a disruption in the balance of the cathodic and anodic reactions and will cause a net current flow from the electronic circuit into the metal sample [48].

The methodology is set forth in the appropriate ASTM standards [23-26] and has also been presented by Gamry, the manufacturer of the potentiostat equipment and software used in this experiment. These methods measure a log current versus potential over a range of about 0.5 V [48]. The voltage scan is centered on the Open Circuit Potential and then the measured data is fit to a theoretical model of the corrosion process [48].

The Tafel equation relates the rate of electrochemical reaction to the potential. Equation 4.2-1 represents the current resulting from the reaction on a single electrode.

$$I = I_0 \exp\left(\frac{2.303\left(E - E^o\right)}{\beta}\right)$$

Equation 4.2-1. The Tafel equation [48].

Where,

I = Current resulting from the reaction
I_0 = Reaction dependent constant called the Exchange Current
E = Electrode potential
E^o = Equilibrium potential (constant for a given reaction)
β = Reaction's Tafel Constant (constant for a given reaction) in volts/decade

However, in a corrosion system both the cathodic and anodic reactions occur, so the two can be combined in Equation 4.2-2, the Butler-Volmer equation.

$$I = I_{corr} \exp\left(\frac{2.303\left(E - E_{corr}\right)}{\beta_a}\right) - \exp\left(\frac{-2.303\left(E - E_{corr}\right)}{\beta_c}\right)$$

Equation 4.2-2. Butler-Volmer Equation [48].

Where,

I = Measured cell current in amps
I_{corr} = Corrosion current in amps
E = Electrode potential in volts

E_{corr} = Corrosion potential in volts
β_a = Anodic Beta Tafel Constant in volts/decade
β_c = Cathodic Beta Tafel Constant in volts/decade

The electrode potential, E, is controlled during the electrochemical testing. The cell current, I, is measured by the potentiostat device. This relationship is used to determine the corrosion current, I_{corr}, which can then be used to determine the corrosion rate. When the electrode potential, E, is equal to the corrosion potential, E_{corr}, the cell current will be zero because each of the exponential terms will be one. When the potential is near E_{corr}, both of the exponential terms contribute to the overall current, but as the potentiostat pushes the potential farther from E_{corr}, one of the exponential terms will dominate and the other can be ignored [48]. When this happens, the plot of log current versus potential becomes a straight line [48]. This is shown in Figure 4.2-1.

The potential can also be plotted as a function of the log current density, i_{corr}, in units of Amps/cm^2 [10]. The corrosion density is calculated by dividing the total current by the geometric area of the electrode exposed to the solution; this assumes that the current is distributed uniformly across the surface [26]. Equation 4.2-3 shows the relationship between corrosion current density and corrosion current.

$$i_{corr} = \frac{I_{corr}}{A}$$

Equation 4.2-3. Corrosion current density [26].

Where,

i_{corr} = Corrosion current density in $\mu A/cm^2$
I_{corr} = Total anodic current in μA
A = Exposed specimen area in cm^2

In order to use polarization resistance to measure the corrosion current, I_{corr} (or corrosion current density, i_{corr}) these parameters can be directly related to the polarization resistance, R_p. Here, the voltage is plotted as a function of current as the cell voltage is "swept over a small range of potential that is very near to the E_c (generally ± 10 mV) [48]". When restricting the potential near E_{corr}, the current versus voltage curve is approximately a straight line whose slope is the polarization resistance, R_p, in units of ohms. This follows Ohm's Law, R=V/I. The Equation 4.2-4 shows this relationship, in which the corrosion current density can be used interchangeably if the units are adjusted accordingly.

$$R_p = \frac{\beta_a \beta_c}{2.303(I_{corr})(\beta_a + \beta_c)}$$

Equation 4.2-4. Polarization resistance [10, 48].

Because the polarization resistance, R_p, is measured, it is possible to find the corrosion current, I_{corr}, if the beta values are known. Once the I_{corr} value is determined, Faraday's law can be used to calculate the corrosion rate in terms of penetration rate (CR) or mass loss rate (MR) [26]. The equivalent weight, EW, is "the mass of metal in grams that will be oxidized by the passage of one Faraday (96,489 ± 2 C (amp-sec)) of electric charge [26]." Equation 4.2-5 shows the equivalent weight calculation for pure elements.

$$EW = \frac{W}{n}$$

Equation 4.2-5. Equivalent weight [26].

Where,

EW = Equivalent weight; value of EW is not dependent on the unit system chosen so it may be considered dimensionless
W = Atomic weight of the element
n = Number of electrons required to oxidize an atom of the element in the corrosion process (the valence of the element).

Equivalent weight is used in the calculation of the corrosion rate and the mass loss rate, shown in Equation 4.2-6 and Equation 4.2-7.

$$CR = K_1 \frac{i_{corr}}{\rho} EW$$

Equation 4.2-6. Penetration rate in units of mm/yr [26].

Where,

CR = Corrosion (penetration) rate in mm/yr
i_{corr} = Corrosion current density in μA/cm^2
K_1 = Constant 3.27×10^{-3} mm-g/(μA-cm-yr)
ρ = Density in g/cm^3
EW = Equivalent weight; value of EW is not dependent on the unit system chosen so it may be considered dimensionless

$$MR = K_2 i_{corr} EW$$

Equation 4.2-7. Mass loss rate in units of g/m^{2}d [26].

Where,

MR = Mass loss rate in g/m^{2}d
i_{corr} = Corrosion current density in μA/cm^2
K_2 = Constant 8.954×10^{-3} g-cm^2/(μA-m^2-d)
EW = Equivalent weight; value of EW is not dependent on the unit system chosen so it may be considered dimensionless

The corrosion current density, i_{corr}, can be replaced with the corrosion current, I_{corr}, according to the definition of i_{corr} given in Equation 4.2-3 if the units are adjusted for the K constants.

Table 4.2-1 can be used to convert units in the two equations, ultimately resulting in quantitative corrosion rates.

Table 4.2-1. Values of constants for use in Faraday's equation [26].

A				
Penetration Rate Unit (CR)	I_{corr} Unit	ρ Unit	K_1	Units of K_1[A]
mpy[C]	μA/cm^2	g/cm^3	0.1288	mpy g/μA-cm
mm/yr[B]	A/m^{2B}	kg/m^{3B}	327.2	mm kg/A-m-yr
mm/yr[B]	μA/cm^2	g/cm^3	3.27×10^{-3}	mm g/μA-cm-yr

B			
Mass Loss Rate Unit (MR)	I_{corr} Unit	K_1	Units of K_1[A]
g/m^{2}d[B]	A/m^{2B}	0.8953	g/Ad
mg/dm^2(mdd)	μA/cm^2	0.0895	mg cm^2/μA-dm^2-d
mg/dm^2(mdd)	A/m^{2B}	8.953×10^{-3}	mg m^2/μA-dm^2-d

[A]EW is assumed to be dimensionless
[B]SI unit.
[C]mpy is milli-inches per year.

4.2.2.2 Electrochemical Cell

Electrochemical testing is normally set up with an electrochemical test cell that is connected to a computer-controlled potentiostat, which controls and measures the voltage or current in the test cell. The cell itself is a container made of a material that will not corrode, deteriorate or contaminate the test solution in any way, such as a glass flask [25]. The cell is then filled with an electrolyte solution, into which three electrodes are immersed: the working electrode, the counter electrode, and the reference electrode. For these tests, the working electrode is the metal coupon of silver, lead or copper, on which the corrosion will occur. The counter (auxiliary) electrode in this case is platinum. The counter electrode acts to complete the cell circuit when voltage is applied, and being more noble, it will act as a cathode. The varying potential differences between the metals of the working and counter electrodes creates an open circuit potential through the electrolyte solution. The reference electrode, in this case Silver/Silver Chloride, does not conduct current, but acts as a known electrode potential in the system. The electrolyte, in the present experimental setup, is an extraction from the material to be tested. In an

electrochemical experiment, the open circuit potential is found by measuring the potential of the working electrode compared to that of the reference electrode. It is important that the reference electrode is well characterized and stable, because error and damage in the reference electrode will affect all measurements taken during testing.

4.2.2.3 Extractions

Electrochemical corrosion testing looks at the corrosion incurred by a working electrode immersed in a corrosive environment when the voltage conducted through the cell is controlled to mimic effects of aging. In order to perform the tests, the corrosive environment must be translated into an aqueous medium used as the electrolyte solution of the electrochemical cell. This is comparable to the simulated 100% relative humidity of the Oddy test environment.

The idea of the extraction in this type of testing is that it represents an environment rife with the potentially harmful ions that may form from the material in question on the moist surface of a nearby metal. The extraction introduces ions to the metal, as well as conducts the charge necessary for corrosion reactions. For the brominated FRs, it is expected that the electrolyte solution will be filled with bromine ions from the redox reactions discussed earlier. These ions may potentially react with the metal acting as the working electrode in the electrochemical cell.

4.2.2.4 Potentiostat Device

A potentiostat device allows for control of the electric potential (voltage) between the working electrode and the reference electrode in an electrochemical cell [48, 49]. In effect, it allows the user to measure the potential difference between the working and

reference electrode. It also allows the user to force the necessary amount of current to flow between the working and counter electrodes to hold a desired potential. By comparing the potential difference to a preset voltage, the potentiostat will force a current through the counter electrode towards the working electrode. This will counteract the difference between preset voltage and existing working electrode potential [49].

Figure 4.2-2 shows a simplified schematic of the potentiostat. The "X1" markings on the amplifier indicate that it is a unity gain differential amplifier, which means that the output voltage from this circuit is the difference between its two points [48].

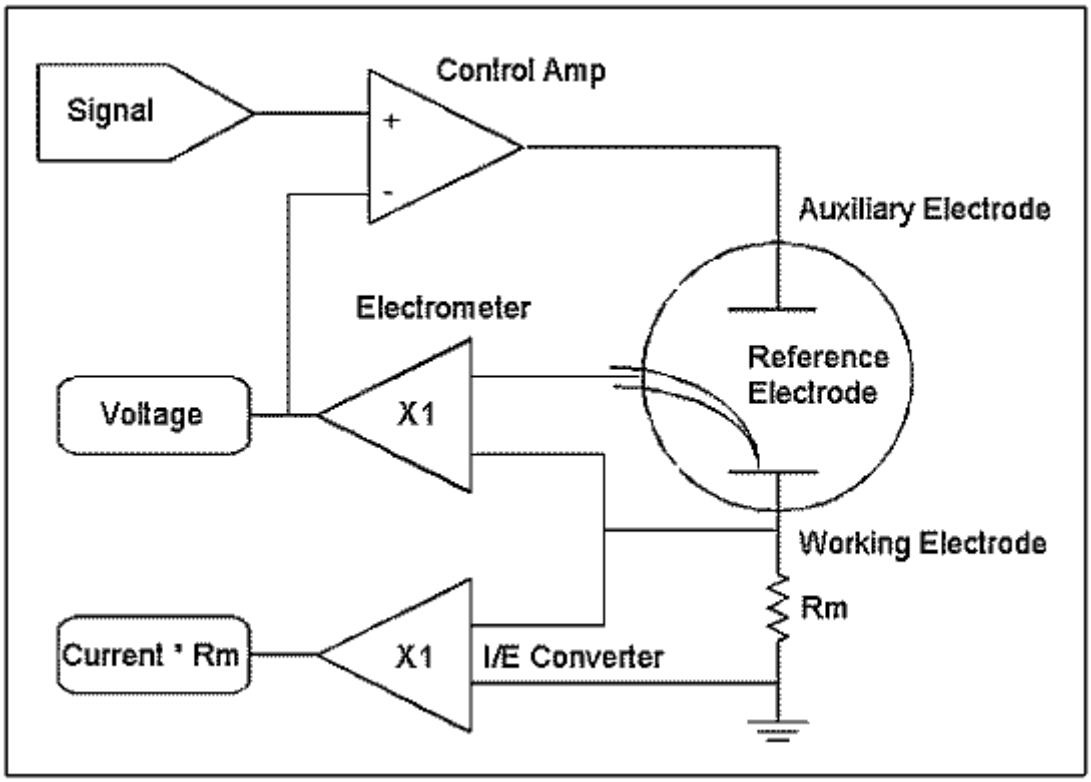


Figure 4.2-2. Simplified schematic of Gamry Instruments' Potentiostat [48].

This schematic shows four circuit blocks; the electrometer circuit, the I/E converter circuit, the control amplifier circuit, and the signal circuit. The electrometer circuit measures the difference between the reference and the working electrodes. It is

the feedback signal in the potentiostat circuit and it is the signal that is measured to get the cell voltage [48]. The I/E converter circuit converts current to voltage and measures the cell current in doing so. The I/E converter forces the cell current to flow through a current measurement resistor, R_m, across which the voltage drop is a measure of the cell current [48].

The control amplifier is a servo amplifier, meaning it can be controlled through feedback. It allows for the cell voltages to be made equal by comparing the measured cell voltage to the desired voltage and then driving current into the cell to match the voltages [48]. The signal circuit is a voltage source controlled by the computer in which the potentiostat device has been setup. The digital-to-analog (D/A) converter is where the output is converted from computer generated numbers into voltages [48].

4.2.3 Other Tests

4.2.3.1 Weight Change

As stated in Bernt, the "metal corrosion rate is commonly determined by exposing a cleaned test coupon with known surface area and weight to the conditions of interest for a length of time, removing the salt formed by an appropriate method, and determining the weight loss [17]." The corrosion weight is found by dividing the measured weight loss by the exposed surface area and the exposure time [17]. By the same token, if corrosion salts formed on a coupon do not dissolve or otherwise separate off,, the weight gain can be used for the same calculation. Measuring the gain in weight is often easier because it does not require the removal of corrosion spots, which can be difficult to measure on small coupons.

This test method implies that the weight gain from corrosion is constant over time, when in reality it is probably not. As the salt layer builds up, a type of passivation occurs where "the reactants for the corrosion reaction have to diffuse through an increasingly thick salt layer to reach the reaction sites [17]."

4.2.3.2 pH

By testing the acidity of a material, it is possible to gain some knowledge about how corrosive it might be to metals. Acids are generally very reactive with metals, forming a metal salt (corrosion) and hydrogen. Hydrochloric acid (HCl) is a strong acid, and the similar hydrobromic acid (HBr) is even stronger. Using the extractions discussed earlier in the electrochemical testing procedures, it is possible to measure pH. A pH lower than 7.0 indicates that the extraction is acidic, and that the material extracted may not be safe for use around metal artifacts.

4.2.3.3 Azide Test

In this test procedure, a sodium azide based solution is observed to decompose when in contact with materials with the potential to tarnish silver by evolution of hydrogen sulphide [16]. The test is performed by using a very small sample of the material that might be damaging and observing it under a microscope at 40x magnification with the addition of the sodium azide solution. The sample is observed for about a minute and an assessment is made regarding the amount of nitrogen bubbles that form during this time [16]. The more bubbles that form, the more serious the tarnish on silver is expected to be. This test is quick and easy, but is only good for information about silver.

4.2.3.4 Iodide/Iodate Test

This test is another way to find out if a material is releasing acids. It is based on the reaction of acids with iodate and iodide ions to produce iodine. Iodine can be detected because it reacts with starch and produces a blue-violet color that is easily identified [19]. To perform this test, iodide, iodate and a starch solution are placed in a reaction dish which is suspended inside of a larger reaction flask, shown in Figure 4.2-3.

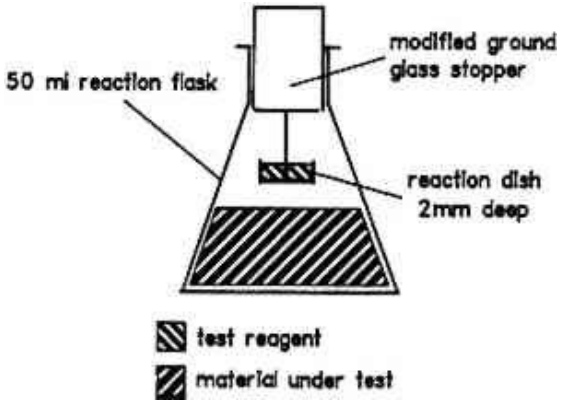


Figure 4.2-3. Iodide/Iodate reaction flask [19].

The material to be tested is then added to reaction flask, and the entire flask is sealed and placed in an oven at 60 ºC for about 30 minutes. If the contents of the reaction dish have turned blue-violet in color, then this shows the presence of volatile organic acids and indicates that the test material should not be used for most museum applications. This test is probably better than a simple pH test because, rather than looking only at the aqueous extractions, it allows for the vapors to be emitted in a way more representative of actual museum conditions, although at temperatures close to room conditions.

4.2.3.5 Chromatropic Acid Test

The chromatropic acid test determines if formaldehyde is present by utilizing its reaction with chromotropic acid. Chromotropic acid turns purple when formaldehyde is present, so this test can be run in a manner very similar to the iodide/iodate test. The

same test apparatus, shown in Figure 4.2-3, is used, but the reaction disk is instead filled with the chromotropic acid solution. The same test procedure can be followed as that of the iodide/iodate test discussed earlier [19].

4.2.3.6 Beilstein Test

The Beilstein test is generally used to detect halogens in plastics. The materials required are copper wire, a gas flame, and the plastic to be tested for halogens. The wire is first heated to glowing to remove any dirt or other materials that will introduce potential error. A small amount of the plastic is put on the end of the wire, and then this end is exposed to the gas flame. If the plastic contains chlorides, the flame will turn bright green, and if bromine or iodine is present, the flame will turn a bright blue color. This is a quick way to determine if halogens are present, because halogens are generally avoided as a precaution against corrosion.

4.2.3.7 XRF

X-ray fluorescence (XRF) analysis detects the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays. With XRF, it is possible to determine which elements are present in a material, although lighter elements are generally no detected. This test method requires more expensive equipment and expertise to interpret the results. However, this test procedure provides rapid and definitive identification of many elements, including Bromine and Antimony. Identification of chlorine, and possibly phosphorus, can be accomplished with vacuum capability and appropriate filters and beam settings.

Chapter 5 Experimental Testing Procedures

5.1 Test Methodology

5.1.1 Burn Test

Small scale burn tests were performed to assess the burning characteristics of the various types of polyethylene sheeting being investigated. Video footage was taken, and temperature has been measured during each test. The tests were meant to simulate a sheet of plastic being draped over an artifact, representing a situation that might occur during renovations in a museum space, or in a storage unit as temporary or long-term protection against leaks. A small ceramic sculpture, roughly a 6-inch cube, was used as the mock artifact. It was covered with tin foil prior to each test to ensure that no leftover remnants of plastic would interfere with the test, and placed on a pedestal that was also covered in foil. The foil-covered statuette was draped with a 1'6" by 1'6" sheet of plastic and a small flame was introduced at the lower corner edge of the draped plastic to cause ignition.

This experiment demonstrated how the plastic sheeting would react to ignition and how the artifact would be affected by the plastic if exposed to a small flame. This test was not performed in order to gather quantitative data, but rather to observe the process of flame spread and how the "artifact" would be affected by the plastic and heat. The experiment was performed under a hood because a large volume of smoke was expected when the plastics did burn and the composition of volatiles was unknown. Each test was videotaped for review. Observations were recorded regarding the ease of ignition, the quality of the smoke produced and the speed of the flame spread.

The time to ignition was recorded using video; however, this data is not presented because many of the flame retardant plastics took a very long time for ignition to occur, and more than one attempt in all FR cases. Temperature measurements were taken using two thermocouples, one located beneath the plastic cover (coming through the hollow statue) and the other positioned 10 inches above the statue setup. The temperatures were recorded continuously during attempts to ignite the plastics. In all cases, the FR plastics eventually ignited, but they would generally self-extinguish rapidly; this scenario did not allow for good temperature measurement.

5.1.2 Oddy Test

5.1.2.1 Overview of Method

The Oddy test was performed using the modified three-in-one method described in the paper by Bamberger et al. [8]. The advantage of this method was its simplicity and the availability of the materials needed. The test utilized 1.25 inches by 0.5 inch silver, copper and lead coupons in order to allow for the largest possible surface area of exposure in this setup, and to optimize for visual and XRF analysis.

The test containers used were wide-mouthed flint-glass jars, 6 cm in diameter and 5.4 cm high, with a volume of 135 ml. They come with polypropylene screw-fitted lids with a Teflon fluoropolymer resin liner, which fit tightly against the mouth of the jar and separated the lid from the contents of the container. The sample holder used was a 10 ml pyrex glass beaker. The setup for this method can be seen in Figure 5.1-1.

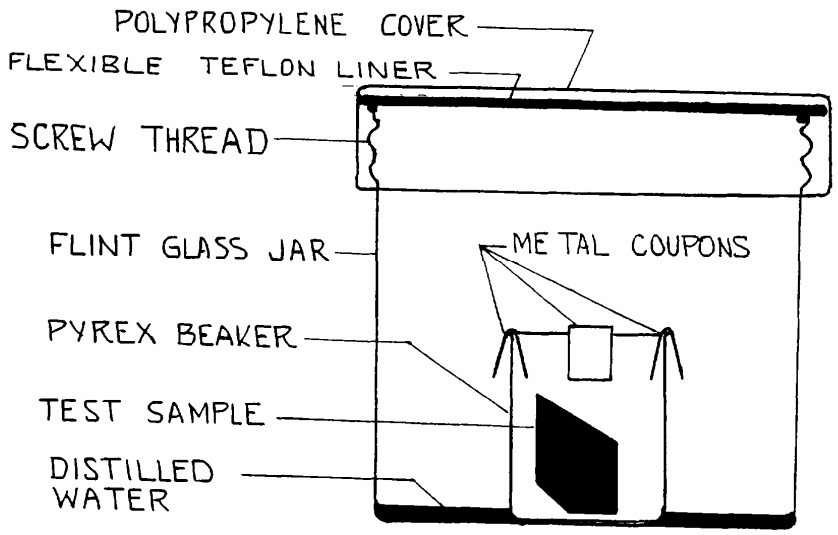


Figure 5.1-1. Three-in-one Oddy test setup with threaded glass jar and cover [8].

5.1.2.2 Procedure

All jars and lids were first cleaned thoroughly using laboratory cleaning solvent and distilled water, then were allowed to air dry. After being cleaned, the containers and lids were handled only with gloved hands or tweezers.

The silver and copper coupons were each polished using several grades of Micro-Mesh cloths and cleaned with propanol solvent to remove any remaining oils. Micro-Mesh cloths are finely grained abrasives. Polishing was performed by applying gentle pressure in one direction, and then turning the metal 90º and polishing in one direction again. The coarseness of the abrasive was chosen based on the hardness of the metal and the amount of tarnish and corrosion already present. The goal of the polishing procedure was to create a smooth, clear and uniform surface from coupon to coupon in order to ensure a controlled test method.

The silver coupon metal was cut from sterling silver sheet with a purity of 92.5%. The copper coupons were cut from 99.99% pure copper sheet metal. The lead was a soft

foil of unknown purity. The silver was first swabbed with propanol, then was polished beginning with the 4000 grade Micro-Mesh and increasing gradually to 6000, 8000 and 12000 until all previous spots of visible corrosion and etching were removed. The same procedure followed with the copper, except that because the condition of the copper was better than the silver, the polishing started at 6000 grade and went from there up to 8000 and 12000. Because the lead used was very soft and crumpled, it was smoothed out with a propanol soaked swab, and no polishing with the abrasive cloths was attempted. Once appropriately cleaned, the metals sheets were cut into 1.25 in. by 0.5 in. coupons.

The sheets of sample plastics were rinsed with de-ionized water prior to confetti-cutting into very small pieces to maximize surface area. Each sample holder beaker, except for the control blank, was filled with 1.0 ± 0.005 g of the confetti-cut plastic. Two samples of each of the five types of plastic were prepared, including two blank control jars, totaling 12 sample holder jars.

The cut metal coupons were cleaned a final time with a propanol soaked cotton swab and allowed to dry. Each metal was weighed to ± 0.005 g accuracy, and then one of each type of metal was folded over the edge of each of the sample holder beakers. The metal coupons were not allowed to directly touch the plastic inside of the sample holder beaker. The larger screw-top jars were each filled with 2 ml of distilled, de-ionized water, and the smaller sample holder beakers containing the plastic and metal coupons were carefully placed inside the larger jar, according to Figure 5.1-1. The metal coupons were larger than they appear in this schematic; however, they were still small enough that they did not directly touch the water at the bottom of the jar.

Once the contents of the jar were assembled, the lid was applied and tightened. Each jar was labeled with its contents and sample number. The entire sample was weighed to determine if any moisture was being lost over the course of the heating period. The sample jars were all placed on a tray and were inserted into a laboratory oven, held constant at 60 °C. The jars remained in the oven at this constant temperature for 4 weeks (28 days), and at the end of this time, all jars were removed and allowed to cool. The jars were all weighed prior to being opened to assess the amount of leakage. Once opened, each metal coupon was weighed and visually assessed for corrosion.

5.1.3 Electrochemical Testing

5.1.3.1 Cell Design

The electrochemical cell can be designed in any number of formats as long as it includes a space to hold the extracted electrolyte solution, which must come into contact with the working, counter and reference electrodes and their respective connections to the potentiostat device. The working electrode is the metal being tested (copper, silver, or lead). It is important that only a controlled and known surface area of this electrode be exposed to the solution. The optimal design would only require a very small amount of electrolyte extract solution and minimal amounts of metal for the working and counter electrodes, especially since the counter electrode, platinum, is expensive. The best electrochemical cell setup should be small, easy to clean when the electrolyte solutions are switched, easy to assemble from equipment already available in most labs, and should require minimal materials for testing (such as metals and electrolyte solution).

There are many ways to build an electrochemical cell, but with these design criteria in mind, the final design for this experiment included a tube-like piece of

glassware that could be clamped down against the metal of the working electrode, as shown in Figure 5.1-2. The tube was held against the working electrode metal sample supported by a rubber cork; the metal/glass interface was sealed with silicone grease to prevent leakage. The glass tube had an open diameter of approximately 0.9 cm and a height of approximately 2.7 cm.

Figure 5.1-2. Glassware being clamped to working electrode; rubber cork is being used to hold the WE in place.

This setup allowed the potentiostat to be connected to the working electrode (WE) from the outside of the cell with the alligator clip, shown in Figure 5.1-4. The WE used in the majority of tests was a thin copper coupon. In order to control the surface area of the WE exposed to the electrolyte solution, plater's tape was used. The glass tube could

simply be clamped to a bare piece of metal acting as the WE, however, if small amounts of the electrolyte solution were to drip outside of the tube diameter, the known corroding surface area would be compromised. The plater's tape was used in order to control the leakage and spread of the exposed surface area of the working electrode. The plater's tape used in this experiment, is a chemically inert vinyl tape from 3M that can be used for applications such as metal plating which involve exposure or resistance to chemical environments. It is therefore ideal for the purposes of electrochemical testing. By punching a hole with a known area through a small swatch of the linered tape, then sticking it to the metal coupon, only a controlled surface area of the WE is exposed to the electrolyte solution, as is shown in Figure 5.1-3. The tape-covered region of the metal coupon was protected from contact with the aqueous solution and was protected from corrosion. The exposed surface area was limited to 0.3 cm^2 for this testing.

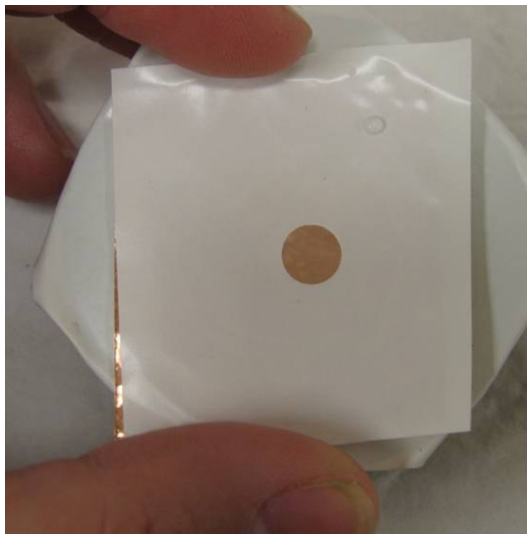


Figure 5.1-3. Controlled surface area of working electrode through use of hole-punched plater's tape.

The tape can be peeled back on the region of the metal coupon outside of the cell, around the lip of the tube to allow room for the potentiostat WE hookup, shown in Figure 5.1-4.

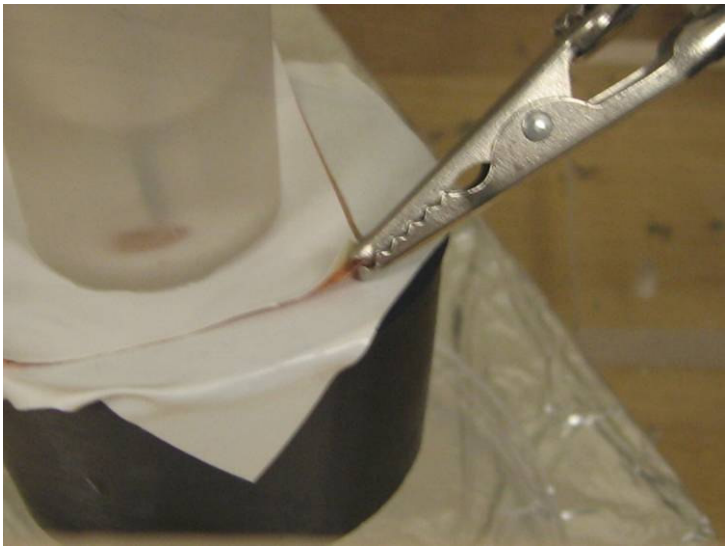
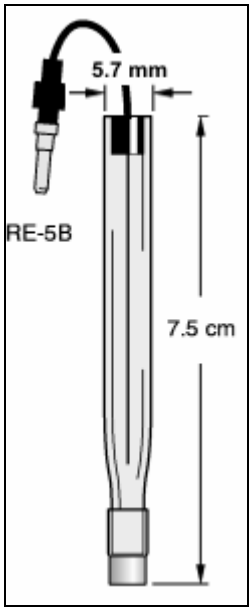


Figure 5.1-4. Working electrode hookup to potentiostat (alligator clip), using the outside edge of the coupon.

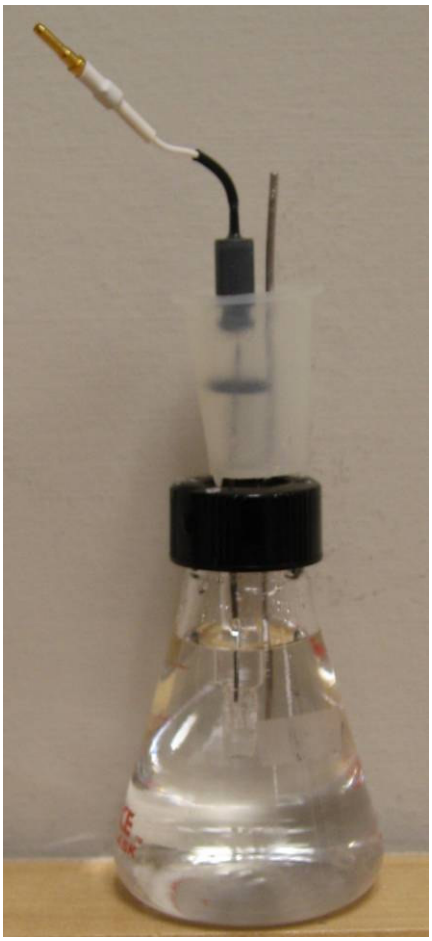
The reference electrode (RE) and counter electrode (CE) could then be inserted from the top of the tube into the solution. The amount of the metal needed for the WE could be as little as a 1.5-inch square coupon, cut from the same material used for the Oddy test. Because the metal can be cleaned and re-polished between each test, only a few coupons of each metal are needed. Less than 4 ml of electrolyte solution are required to run the test, along with a small length of platinum wire to be used as the counter electrode (CE), and a thin reference electrode (RE) which would need to be purchased at a minimal price.

The RE used in this test was a silver/silver chloride electrode in a glass vile containing a filling solution of aqueous 3 M NaCl saturated with AgCl ordered from BASi (http://www.bioanalytical.com). A schematic of the dimensions of the electrode are shown in Figure 5.1-5(a). The RE included a vycor frit at the solution interface held in place by a plastic heat-shrink tube. The vycor frit allows the electrolyte solution to mingle with the contents of the RE. When not in use, the RE was stored in a 3 M NaCl solution, shown in Figure 5.1-5 (b), in order to ensure its functionality. A special lid was

designed to allow the reference electrode to fit snuggly in the storage flask and to ensure that it was properly immersed in the buffer solution, not touching the bottom of the holding glass, which could have caused damage to the frit.



(a)



(b)

Figure 5.1-5. (a) BASi Ag/AgCl reference electrode, model RE-5B., (b) shown in 3 M NaCl buffer solution.

A small length of platinum wire was used as the CE. The stiff platinum wire and reference electrode were inserted through holes in a specially made cap and were both connected to their respective alligator clip connections to the potentiostat. The platinum wire can be seen in Figure 5.1-6, beside the electrode. In order to get a good current running through the electrochemical cell, it is important to have the RE and the CE close to the WE, and held at constant locations for each test. In order to ensure this

positioning, the CE and RE were fitted through the cap shown in Figure 5.1-7 (a) in such a way that the tip of the RE and the tip of the platinum CE would always be close to one another as shown in Figure 5.1-7 (b).

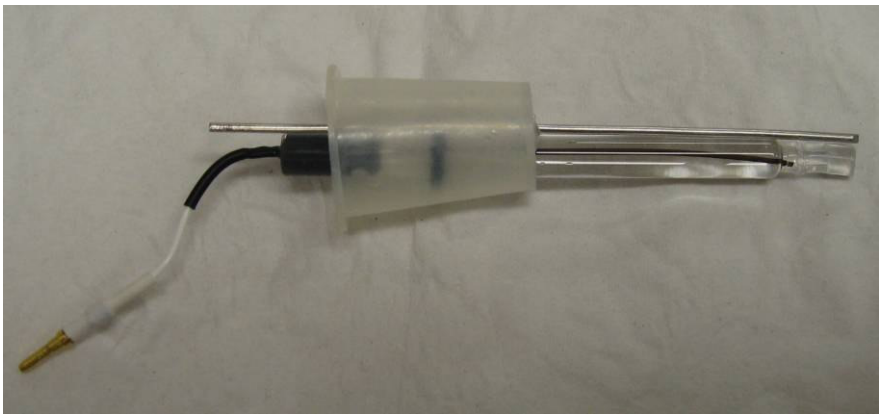
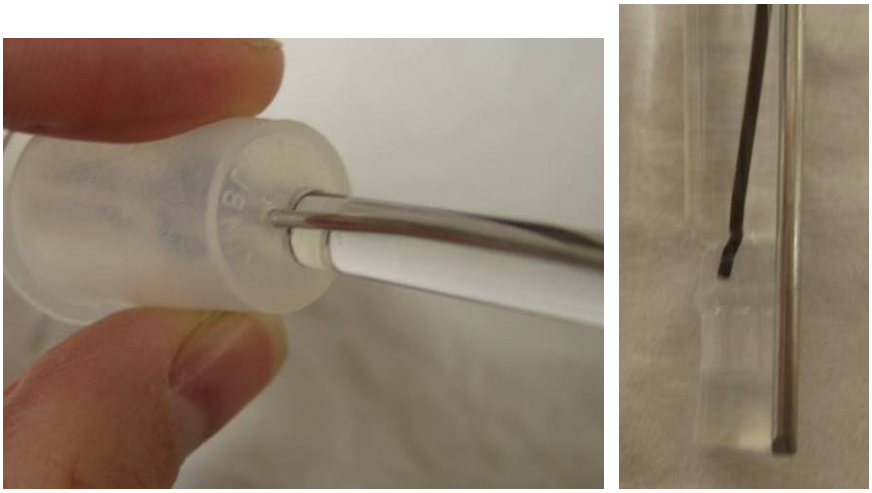


Figure 5.1-6. Platinum counter electrode and Ag/AgCl reference electrode through holder tube.



(a) **(b)**

Figure 5.1-7. RE and CE fitted through cap (a) so that the tips of each are close together during testing(b).

The complete cell setup, shown in Figure 5.1-8, is a simple design that was easy to assemble and disassemble, and inexpensive. The WE metal was first polished, and then the plater's tape with punched hole was applied. The covered metal was clamped into place between the glass tube and the rubber cork with a clamp. About 2-3 ml of electrolyte solution was poured into the glass tube, and the cap holding the RE and CE was placed in the tube and adjusted so that the RE and CE were directly above the

exposed WE surface. The three electrodes were connected to their respective leads to the potentiostat device so that testing could begin.

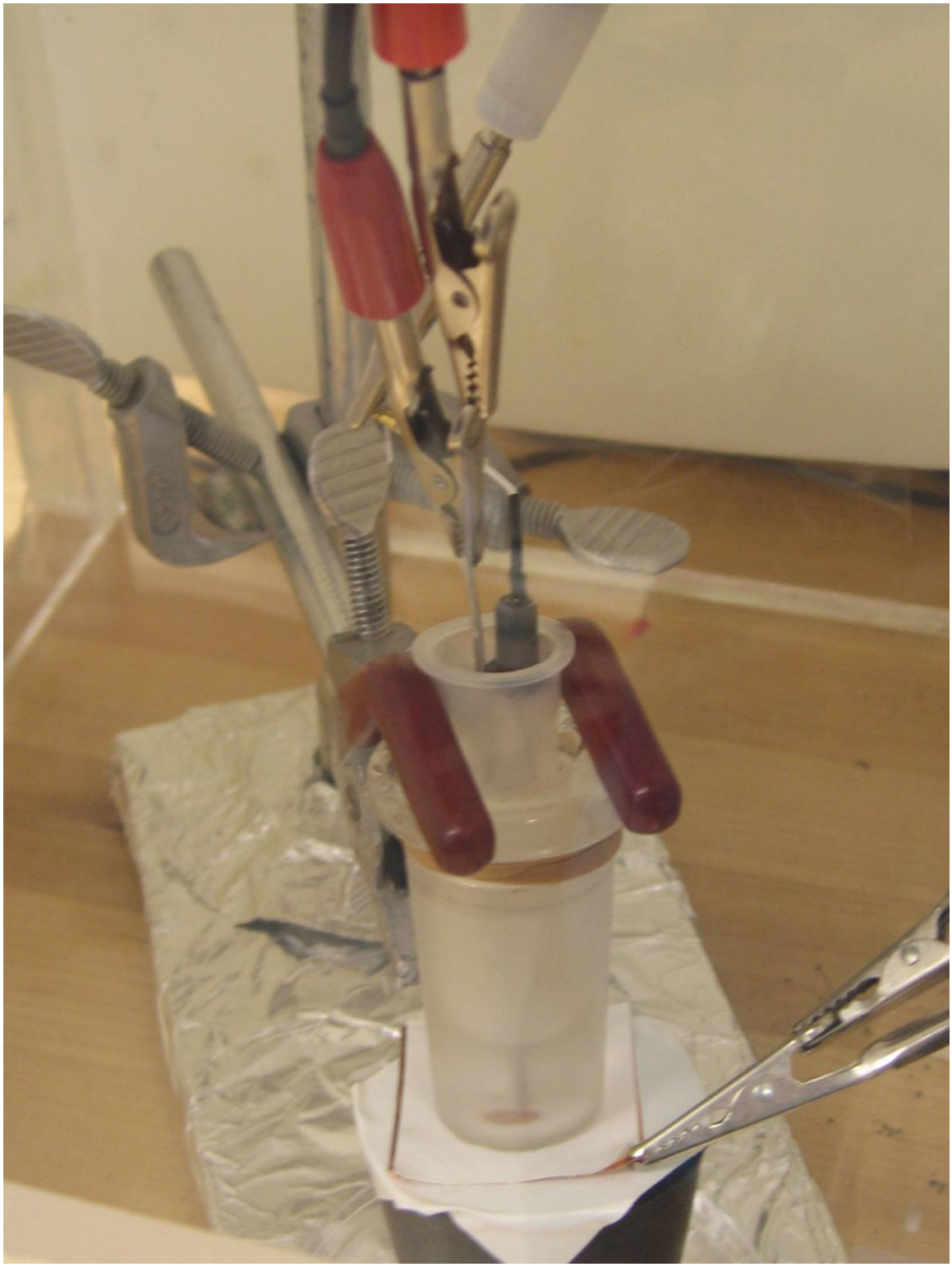


Figure 5.1-8. Electrochemical cell setup.

The colored alligator clips seen in the pictures are the hookups to the Gamry Potentiostat. The seven hookups are color-coded according to which part of the cell they connect. The working sense (blue) connects to the working electrode (green), which attaches to the edge of the WE metal clamped at the base of the electrochemical cell. The counter sense (orange) connects to the counter electrode (red), which is connected to the platinum wire acting as the CE. The reference electrode (white) clip connects to the reference electrode plug. Figure 5.1-9 shows the color-coding of the alligator-clip hookups.

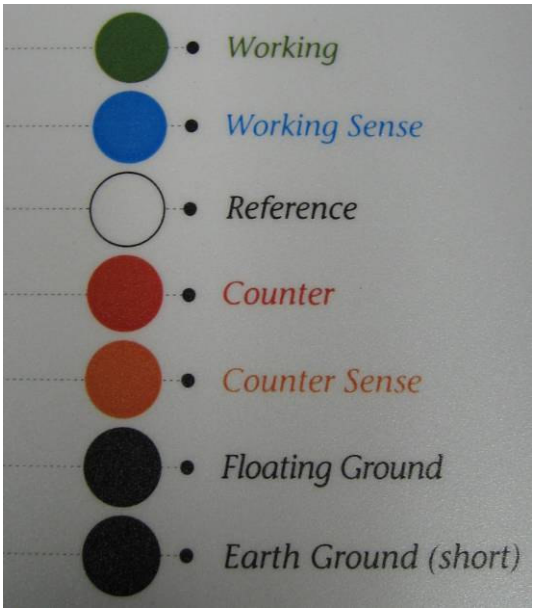


Figure 5.1-9. Electrode hookup reference colors.

The cell needs to work in a fairly stable environment; i.e. temperature and humidity must be steady. In order to control the ambient conditions, the cell was assembled in a sealable Plexiglas box, which was outfitted with a temperature and humidity monitor. Because the lab in which testing took place tended to have significant fluctuations in temperature and humidity throughout the day, a foam layer was added on the outside of the box in order to further minimize temperature change. The foam

covered box is shown in Figure 5.1-10. The stand used to hold the clamped cell setup and the connector wires in place are also shown.

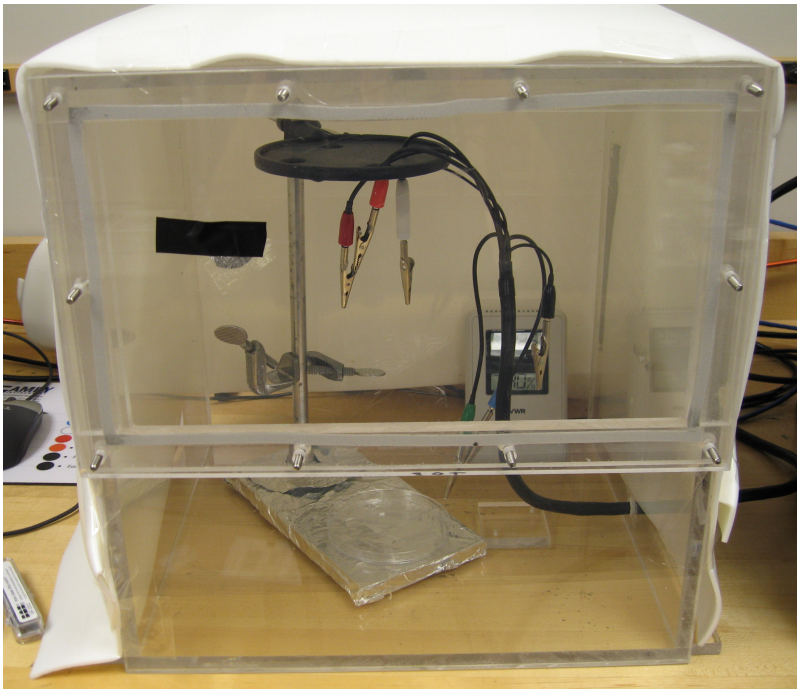


Figure 5.1-10. Foam-coated Plexiglas box containing cell setup.

5.1.3.2 Extraction Procedure

In order to translate the presence of fire retardant treated plastics in a humid environment, aqueous extractions of the plastics were made. Because plastics are generally impermeable to water, determining whether the extraction procedure was effective was difficult. The lab procedure used was a modified version of ASTM C871-95, the Standard Test Method for Chemical Analysis of Thermal Insulation Materials for Leachable Chloride, Fluoride, Silicate, and Sodium Ions, and the methods described by Reedy, et al. [10, 27]. These test methods extract potentially corrosive species from materials. Although the main chemical species of interest here was bromine, particularly from the polybrominated diphenyl ethers (PBDEs), it was felt that these methods

reasonably represent mechanisms that take place in real-life, worst case scenarios or over time.

It was suggested that organic solvents would be more effective at extracting the brominated molecules from the plastics; however there are a number of problems with this approach. As soon as organic solvents are introduced, the test becomes less realistic. It is likely that there will be moisture from water present in a museum setting, but highly unlikely that there will be organic solvents present in the museum environment. In addition, organic alcohols contain less ions to conduct electricity through the cell. This would make measurements within the electrochemical cell more difficult and would require the addition of conductive salts, which would complicate interpretation of the test results. Due to these problems, this testing focused exclusively on extractions made with ultra-de-ionized (DI) water. The ultra-DI water contributed a negligible number of ions, so that any conduction occurring in the cell was assumed to come from the extracted material.

In overview, the extraction method consisted of weighing out a certain mass of each plastic, which had been cut up into smaller pieces to maximize surface area, and placing the plastic sample into a specified volume of ultra-DI water. These mixtures where heated for a specified period of time, allowing any ions to leach out of the plastic and into the water, as detailed below.

Two separate extraction procedures were performed: one in which the mixtures were boiled for half an hour, then allowed to cool, and a second procedure in which the mixtures were heated to a steady temperature below the boiling point of both water and bromine in sealed containers for an extended period of time (~72+ hours). This second

test method was chosen because it allowed more control over the loss of vapors from the extraction. Bromine has a boiling point of 58.8 °C, so that there was concern that any bromine extracted from the plastics might boil off with the water vapor. In a sealed container at a temperature below boiling, the bromine may be more likely to leach out of a plastic and remain in the water.

For the first test, 2.0000 g ± 0.0005 g of each plastic were weighed out and combined in clean 250 ml size glass Erlenmeyer flasks with 100 ml of ultra-de-ionized water. Cork stoppers, which had been punched with holes through the centerline of each cork, were used to plug the flasks. Clean pipettes were inserted through each hole, with the narrow dropper side down so that it would be inside of the flask, above the waterline. The larger half of the pipette extended above the cork and stayed outside of the flask while boiling occurred. The use of the pipette through the cork acted as a pressure relief valve and possibly as a cold finger condenser, in order to minimize the losses of liquid extract during the boiling process. The cork was then covered with two layers of aluminum foil to prevent contamination from the cork entering the extraction. Erlenmeyer flasks also act as condensers in their long necks, so in combination with the pipette, little fluid was lost during boiling.

The five flasks were set onto hotplates, and the heat was slowly increased until boiling occurred in all flasks, at approximately 20 minutes. The setup can be seen in Figure 5.1-11. The extractions were allowed to boil for 30 minutes, and then the heat was turned off and they were allowed to cool on the cooling hotplate, steeping as they sat for approximately 45 minutes. Once boiling had stopped, the pipette-corks were removed

and solid aluminum foil-coated corks were replaced as the extractions were allowed to steep. The extractions were allowed to sit overnight.

Figure 5.1-11. Extraction procedure, test 1.

For the second test procedure, glass screw-top containers with plastic lids, which had fitted Teflon liners, were used. The glassware and lids were cleaned and pre-baked in the oven for 24 hours prior to use. For this test, 4 g ± 0.0005 g of each plastic were placed in the containers with 100 ml of ultra de-ionized water. The lids were lined with aluminum foil again to protect against contamination, and the screw threading was wrapped with Teflon tape to ensure a tight seal. The sealed jars, shown in Figure 5.1-12, were placed in a tray full of tap water which had been preheated to 50°C over a hotplate. The hot bath was used to quickly bring the extractions up to the desired temperature,

allowing for easy measurement of the temperatures within the jars (until all the water evaporated). The entire tray was placed into a laboratory oven, which held at 50 °C for approximately 3 days.

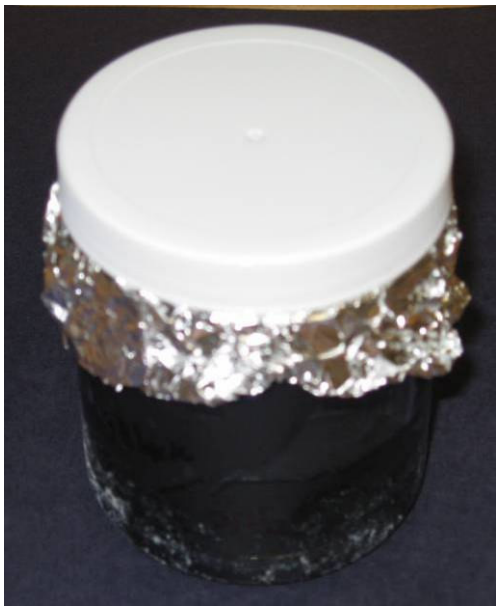


Figure 5.1-12. Second extraction test – jar setup.

A third extraction procedure consisted of using a laboratory microwave was used to quickly bring the mixtures to boiling. The materials extracted in the microwave were not the plastic sheets, but were other materials known to be corrosive to metals, such as plywood and cellulose acetate. The same mass to volume ratio was used in this test. Use of the microwave was assumed to yield comparable or better results for extracting similar amounts of ions from the material being tested.

Microwaving consisted of placing the mixture in the microwave, then allowing the mixture to reach boiling (usually reached in approximately 9 seconds), then stopping and allowing the mixture to cool. This heating/cooling procedure was repeated approximately 30 times. Many of the materials that were extracted in the microwave

produced an excess of particulate, so the resulting liquids were filtered before being tested in the electrochemical cell.

A total of 11 extractions using DI water were used in the final electrochemical test solutions. The ratio of solid to liquid was 1 g mass of the material to 25 mL volume of the ultra-DI water in all solutions, except for the zinc bromide, which contained 6% bromide, a common concentration of bromine in FR plastics. Table 5.1-1 shows the 11 extractions made, and the procedure used for each.

Table 5.1-1. Materials and extraction procedures used.

	Material	Extraction Procedure
1	Ultra de-Ionized Water	– NA –
2	Tap Water	– NA –
3	Polyethylene	Extended Heating
4	ASFR6	Extended Heating
5	DuraSkrim (DSFR)	Extended Heating
6	Blue Deck Cover	Extended Heating
7	BlackFR	Extended Heating
8	Zinc Bromide ($ZnBr_2$)	Mixing and Microwave
9	Plywood	Microwave
10	Cellulose Acetate	Microwave
11	1% Nitric Acid (HNO_3)	– NA –

5.1.3.3 Gamry Instruments Framework Software

The software used to analyze and control data collection using the potentiostat device allows the user to adjust the polarization resistance constraints as needed. To run these experiments, the potentiostat was used to control the voltage through the cell while measuring the resulting current from the varying voltage. The general setup and required inputs for a polarization resistance test can be seen in Figure 5.1-13.

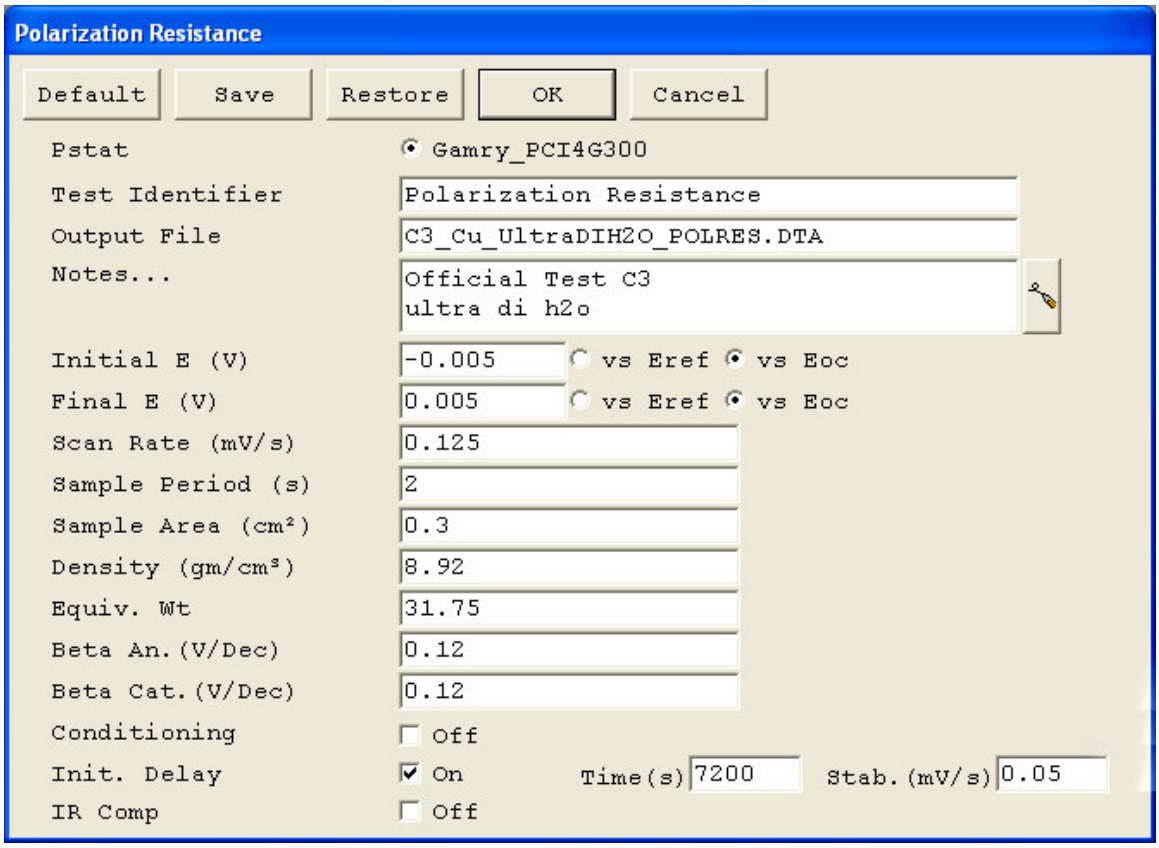


Figure 5.1-13. Gamry Instruments Framework software, Polarization Resistance testing setup window.

To measure the resulting currents while changing the voltage through the electrolyte solution in the cell, the potentiostat device and software are first used to determine the open circuit potential (E_{oc}) of the cell setup, i.e., with no added voltage. The device allows the measurement of voltage with respect to time until a steady equilibrium potential is reached, or until a specified cut-off time. For these experiments, a steady signal was defined as ±0.05 mV/second, or with a cut-off time of 7200 seconds, as shown in Figure 5.1-13. The time to reach E_{oc} varied but generally took between 90 and 300 seconds, so the cut-off time was not necessary.

After the open circuit potential was determined, the potentiostat shifted to the polarization resistance measurement mode. During this procedure, the instrumentation starts at a potential below the E_{oc} and then sweeps up to a higher potential, measuring the

current through the cell at each voltage. The software allows the user to input desired initial and final potentials with respect to the measure E_{oc} value. For the testing procedures followed here, a range of - 0.005 eV to 0.005 eV was used with respect to the measured open circuit potential. The range was initially large, ranging from -0.1 to 0.1 eV, but this produced S-shaped curves, indicating that the range was too wide to determine the straight-line region around the open-circuit potential. By tightening the potential over which the current was measured, it was possible to get a straight-line region from which the polarization resistance could be calculated. The exposed surface area of the WE was also input here (0.3 cm^2), along with a scan rate (0.125 mV/s), sample period (2 s), density of the metal being tested (Cu: 8.92 g/cm^2), and equivalent weight of the metal being tested (Cu: 31.75). The density and equivalent weight inputs could be changed after data collection, if appropriate.

The polarization resistance data collected is displayed in the form of a graph with the current along the x-axis and the potential (voltage) along the y-axis. However, the current was actually the dependent variable, since the potentiostat manipulates the potential, the independent variable. This is a convention of the program, and the axes can be switched if needed. The data appears as a curve with a linear section around the open circuit potential (where I=0.0 A); a region of this line can be selected for the calculation of a slope. The slope of this line, along with the surface area of the WE, the equivalent weight of the sample metal, and the density of the sample are used to determine the corrosion rate, as discussed in Chapter 4.

Another aspect that can be controlled in the program is the conditioning of the specimen prior to testing. When a piece of metal (the WE) is repeatedly polarized and in

contact with a potentially corrosive electrolyte, it may begin to corrode and passivate. As previously discussed, passivation is the formation of a non-reactive surface layer on the WE. The layer is generally a thin oxide layer that will inhibit or slow further corrosion on the sample. In order to reverse this phenomenon and undo some of the damage on the sample, an opposite potential can be run initially through the cell prior to any data collection to reduce the metal surface to a neutral state and remove corrosion. However, it was determined that this added procedure added in too much uncertainty to the results, so conditioning was subsequently eliminated and the coupons were manually cleaned between every 2 or 3 runs of the electrochemical tests.

5.1.3.4 Testing Procedure

The electrochemical cell was set up in accordance with the cell design, discussed earlier. The reference electrode (RE) and platinum wire (CE), secure in the cap holder, were removed from the buffer solution and were rinsed with ultra-DI water in a squeeze bottle, and were soaked in a cup of ultra-DI water, and were again rinsed with the squeeze bottle. The CE and RE were dried with a clean Kimwipe to ensure that no extra liquids could dilute the extraction. This was found to be an important step in the procedure. The RE/CE cap holder was inserted into the open top of the glass, immersing the RE and platinum wire in the extraction solution. The cap holder allowed them to be positioned directly above the exposed copper surface, about 1 mm away. The three electrodes were kept very close, but were not allowed to touch.

Once the setup was in place, each electrode was connected to the potentiostat by its respective alligator clip, discussed earlier. The cords connecting the cell to the

potentiostat ran through a small hole in the Plexiglas box, and to the hookup at the back of the computer. Once all the connections were secure, the Plexiglas box was sealed.

Finally, the Gamry software, discussed earlier, was used to run polarization resistance tests. The polarization resistance test was repeated 3 times for each coupon, without disturbing the setup. The first run was considered to be the actual data, but the second 2 tests were performed to see any trends that might emerge or to detect possible passivation of the metal.

After three polarization resistance tests, the Plexiglas box was opened and the potentiostat hookups were unclipped from each electrode. The RE/CE holder cap was removed from the cell, rinsed, soaked, and rinsed with ultra-DI water, then placed back in the buffer solution holder. The entire cell setup was removed from its ring stand and was taken out of the Plexiglas box to the lab sink where the extraction was dumped out, and the whole setup was thoroughly rinsed with water. The setup was unclamped, and the metal coupon was removed, the glassware was dried with a Kimwipe. The plater's tape was removed from the copper coupon which was then polished and de-greased to be used again. The entire procedure was repeated, usually 8 times for each type of extraction solution.

5.1.4 XRF of Plastic Sheets and Extractions

X-ray Fluorescence was performed by Dr. Lynn Brostoff, with assistance of the author. The analysis is described in an internal Smithsonian report, as follows.

X-ray fluorescence (XRF) spectroscopy utilizes high energy, primary X-ray photons from an X-ray tube to excite electrons in the first three orbitals, called K, L, and M respectively, of the given material on which they impinge. During the excitation and

relaxation processes that result from interaction with the X-ray beam, secondary X-ray photons with characteristic energies are emitted from materials. This phenomenon is called fluorescence. A detector measures the energy of the emitted photons, which are directly related to the elements in the material being analyzed; the signal is shown as spectral peaks when plotted as energy (keV) vs. X-ray intensity (cps).

The instrument used in this analysis was a Bruker Tracer III handheld energy dispersive X-ray Fluorescence spectrometer (ED-XRF). The instrument has a miniature X-ray tube with a Rhodium anode, a Si PiN diode detector, and was operated at two settings: 40 kV and 3 μA , or 20 kV and 0.20 μA using a titanium filter and vacuum. Resolution is typically less than 0.2 keV. For these analyses, the portable XRF unit was used in a stationary mode on a stand. In this configuration, the samples are in good contact with the instrument window. Exposures were set for 120 seconds in order to maximize the signal to noise ratio.

5.1.5 XRD of Coupons and Corrosion Spots

X-ray Diffraction (XRD) was performed by Dr. Lynn Brostoff with assistance of the author. The analysis is described in an internal Smithsonian report, as follows.

X-ray diffraction (XRD) is a non-destructive tool for the identification of crystalline materials such as pigments, ceramics, salts and corrosion. Because of the specificity of crystalline structures, XRD analysis is often definitive in nature. The principles of XRD may be summarized as follows. When X-ray radiation passes through matter, it interacts with the electrons in atoms, resulting in scattering of the radiation. If the material is crystalline, i.e., the atoms are organized in planes, and the distances

between atoms are of the same order of magnitude as the wavelength of the X-rays, diffraction occurs. The diffracted X-rays are emitted at characteristic angles based on the planes between the atoms in crystalline structures. The relationship between wavelength, atomic spacing (d), and angle was solved as the Bragg Equation. This equation allows us to calculate the inter-planar distances in the sample material using the known wavelength of the monochromatic X-rays emitted from the X-ray tube, and the diffracted angle, which is measured by the detector. Each single compound or phase can thus produce a unique XRD pattern or set of "d-spaces," which represent the set of planes that can be passed through the atoms. This pattern can then be compared to sets of d-spaces obtained from standard compounds and is the basis of identification of the material.

The instrument in this analysis is a Rigaku D/Max Rapid. Experimental patterns were produced using Cu Kα radiation, on 0.3 mm collimater 15 minute exposures, at 50 kV and 40 mA. After background subtraction, the patterns were qualitatively matched as well as possible to known materials by reference to patterns in the International Center for Diffraction Data (ICDD) library. Depending on the signal/noise ratio and degree of overlapping of peaks in multiple phases, trace phases may not be detected by this method. Note that all results reported here are qualitative; major and minor phases were only estimated.

5.1.6 pH of Extractions

The pH of a solution is a measure of the concentration of hydrogen ions present in that solution. A lower pH indicates that a solution is acidic by virtue of the presence of more hydrogen ions. In order to look more closely at the relationship between extract pH

and polarization resistance,, and to better understand the extractions taken from the various plastics and other materials, the pH was taken of each extraction.

A pH-meter was used to measure the pH of 11 different solutions in comparison to the pH values of known buffer solutions. The meter uses a glass electrode to measure the activity of hydrogen ions surrounding a thin-walled glass bulb at its tip.

5.2 Sample Plastics

5.2.1 Pure Polyethylene (Freer and Sackler)

The pure polyethylene plastic sheeting used in these tests is the plastic currently used in the Smithsonian's Freer and Sackler Galleries (FSG) and the storage areas associated with the collections there. As discussed earlier, this plastic is used to protect items in storage from the threat of damage from water and dust [2]. The plastic sheeting is about 3 milli-inches thick and clear, and reportedly contains no FR chemicals, as specified for use in museum and archival collections. The plastic samples were supplied by FSG, so that the manufacturer and specifics of the material are unknown. However, pure polyethylene sheeting is fairly standard, so this material is used to represent non-FR polyethylene sheeting that might be used in a museum.

To confirm that the plastic was actually polyethylene, Raman Spectroscopy was used to look at samples of the material. The results of these tests were compared to standard polyethylene spectra, which showed that the plastic is low density polyethylene.

5.2.2 ASFR6

The ASFR6 Cover was obtained from the company Americover, Inc. ASFR6 is a white, anti-static, fire retardant polyethylene plastic that is 6 mil (milli-inches) thick. It

was originally designed to meet the regulations for use in telecommunications facilities, but can be used for a number of other applications. It passes the NFPA 701-99 Test 1 (small scale) standard, and the ASTM E-84 Class A standard, with a Flame Spread rating of 15 and a Smoke Developed Value of 0. It can be used as a protective cover and is also approved for use as a temporary wall partition during renovation.

The actual fire retardant chemical additives used are generally proprietary, and therefore not disclosed to the public.

5.2.3 Dura-Skrim

Dura-Skrim is a pale yellow fire retardant polyethylene sheet plastic reinforced with polyester fibers (called skrim) for extra durability. The plastic is made up of 4 layers which include two outer layers of polyethylene with high concentrations of fire retardant additives, a layer of polyester skrim for durability, and a polyethylene bonding layer to hold the sheet together. This product is manufactured by Raven Industries, Inc. and was obtained from Americover Inc. The Dura-Skrim plastic sheeting came in two thicknesses; 6 mil (DS2FR) and 10 mil (DS10FR). Dura-Skrim meets or exceeds the NFPA 701 Test 2 (large scale requirements).

The material safety data sheets for this product show that the fire retardant chemical additives in thw plastic are brominated diphenyl ethers and antimony compounds.

5.2.4 BlackFR

The BlackFR is a black polyethylene-based plastic obtained from Americover, Inc. with fire retardant additives and a thickness of 4 mil. It passes NFPA 701-99 and -

2004 Test 1 (small scale) and ASTM E-84 Class A with a flame spread of 10, and a smoke density of 40. The MSDS did not contain information about the type of fire retardant additives used.

5.2.5 Blue Deck Cover

The FR polyethylene-based deck cover used in the experiments also came from Americover, Inc. The deck cover is blue in color and has a thickness of 14 mil. This material is manufactured for use by the U.S. Navy as a shipboard protector during construction, overhaul or repair. It is very thick and sturdy, and is not as flexible as the other plastics. It passes NFPA 701-99 and – 96 Test 1 (Small Scale Flammability Test), BS2782: Part1: Method 141; 1986, EN2825 & EN 2826, BS 476: Part 12: 1991 Ignition Source C and Large Flame Test to LPS 1207: 1994 section 3.1.3, as well as Federal GSA Standard 191 Method 5903 FR test (the fire retardant standard required for U.S. Navy approval). The MSDS sheets for this product did not contain the chemical additives used for fire retardance.

Chapter 6 Data Results

6.1 Burn Test

6.1.1 Data Results

The burn test data was produced empirical observations; however, temperature measurements were taken which provide good insight into how the fires were burning. The thermocouples used collected data throughout the ignition process. Because the FR plastics were so hard to ignite, the data acquisition went on for quite some time. Because there was not true control in the exposure time to the ignition source, some of this data is not useful. Except for the pure polyethylene burn tests, time had no relevance in this body of data; however, the data was taken as a function of time. In order not to be misleading, the maximum temperatures achieved are used as a source of comparison between the materials. The maximum temperatures for each test are compiled in Figure 6.1-1 from both of the thermocouples. The polyethylene reaches significantly greater temperatures than those reached by the FR plastics. This can be attributed to the fact that the polyethylene became fully involved in the fire, while the FR plastics did not.

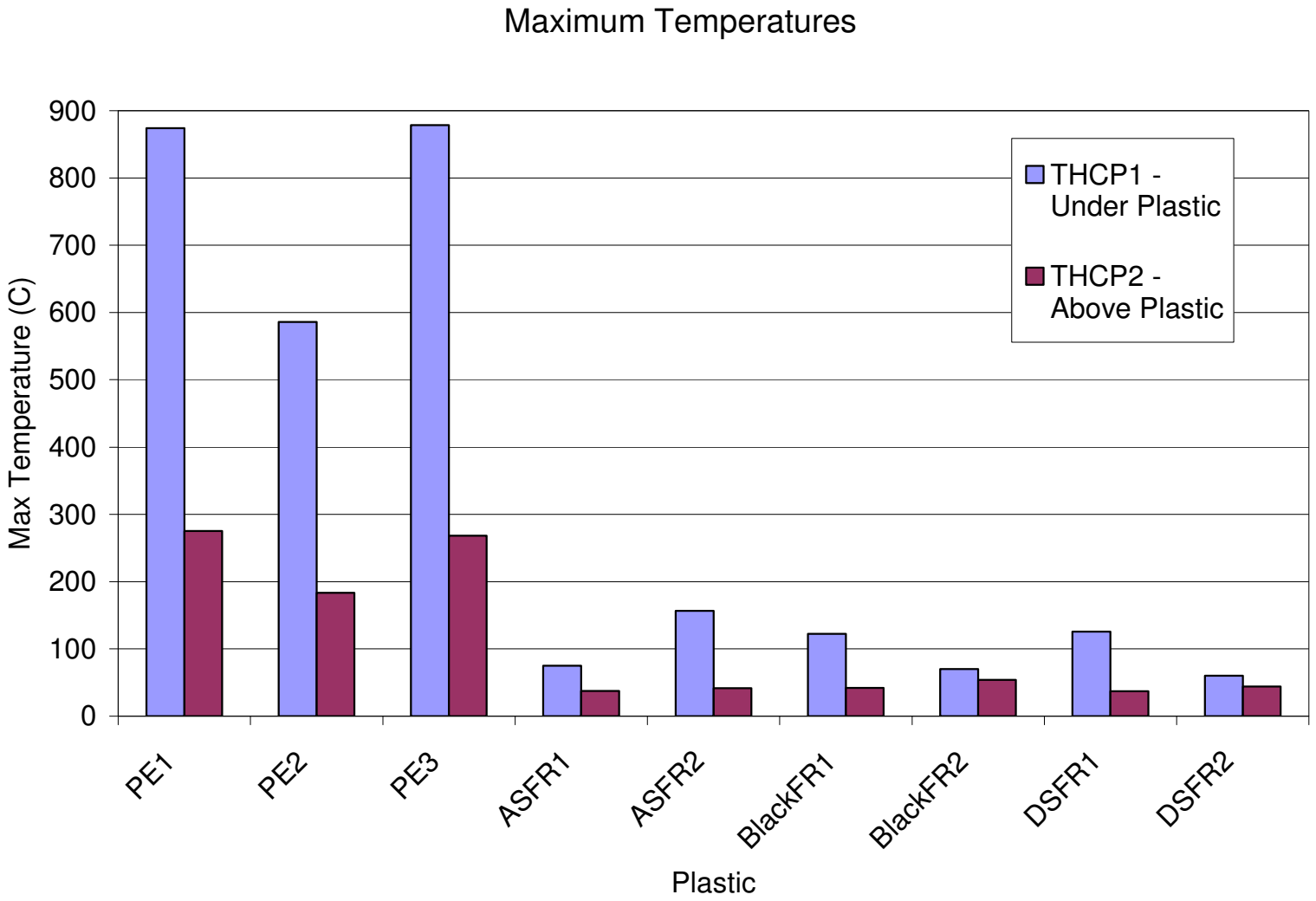


Figure 6.1-1. Maximum temperatures recorded during burn tests.

Because the pure polyethylene was the only material to ignite immediately and to burn until no fuel remained, curve plots of temperature versus time is more informative, as shown in Figure 6.1-2 and Figure 6.1-3. Although data acquisition may have started before ignition, these curves give a good picture of how long it took the fuel load to burn away completely, and how the temperature spikes looked at different locations.

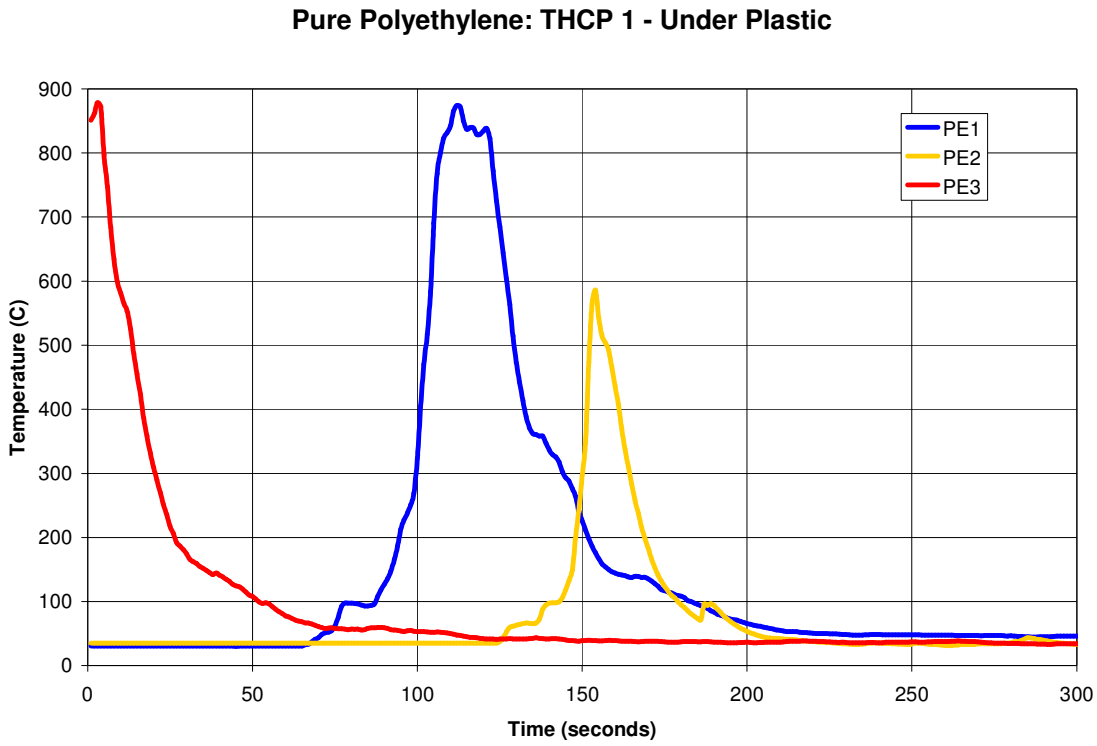


Figure 6.1-2. Thermocouple measurements taken from beneath the plastic cover for pure PE.

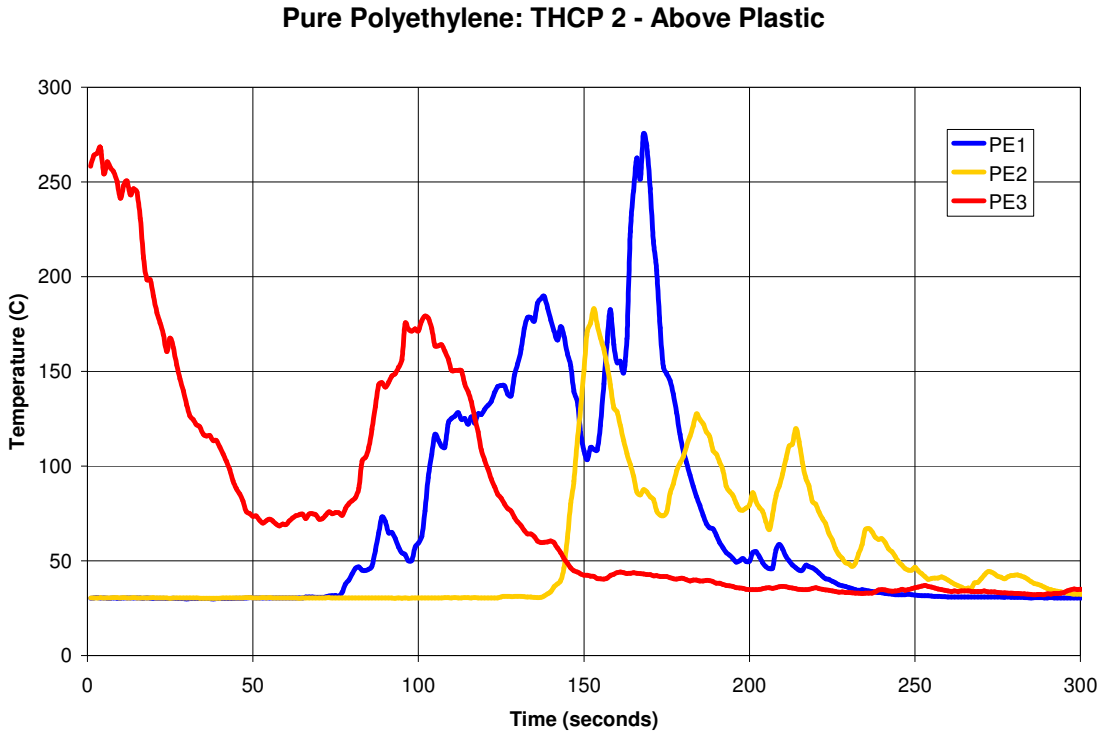


Figure 6.1-3. Thermocouple measurements taken from above the setup for pure PE.

Observations recorded during each test are compiled in Appendix C. The basic observations were that pure PE burned very quickly and produced large flames which would burn until all the plastic was consumed. Overall, the FR plastics were very difficult to ignite. The FR plastics would sometimes begin to burn a little, and a very small flame would be sustained in a limited region for up to a minute, but these flames would always self extinguish. Both types plastics, FR and non-FR produced flaming drips, put most of the pure PE burned away while the drippings from the FR plastics often remained. The FR plastics would sometimes burn better once they had dripped into small puddles.

6.1.2 Data Analysis

Given the small amount of heat being used to ignite the plastics, it is not possible to make conclusive statements about how these plastics will act in a real-life fire situation. However, these tests provided information on small ignition sources and how the FR versus non-FR plastics would affect ignition. These tests also gave information on the maximum temperatures reached from a small ignition source. Table 6.1-1 below shows the average peak temperatures reached for each thermocouple position for the FR plastics versus the pure polyethylene. These temperatures are drastically different, and could mean the difference between a small ignition source growing into a full-fledged fire that might be able to spread beyond its point of origin.

Table 6.1-1. The average peak temperatures for each THCP position for FR vs. Non-FR plastics.

Average Peak Temperatures		
	Under Plastic	Above Plastic
	°C	°C
FR	102	42
Non-FR	780	242

From these tests, it is clear that the flame retardant plastics make a difference in response to a small ignition source. The FR plastics were nearly impossible to ignite, while the non-FR pure polyethylene began to burn immediately as it was touched by flame.

6.2 The Oddy Test

6.2.1 Weighing Test Results

The following data compiled in Table 6.2-1 shows the masses of the metal coupons before and after testing the Oddy Test procedure.

Table 6.2-1. Oddy Test weight measurements from before and after experiment. Total Mass represents the mass of the entire jar configuration and is used to rate the seal – a loss of mass greater than 0.75 grams is considered to be a bad seal, and means that the results are questionable.

	Copper			Silver			Lead			Total Mass			
	Before	After	Corrosion Mass	Before	After	Corrosion Mass	Before	After	Corrosion Mass	Before	After	Mass Loss	Seal?
	g	g	g	g	g	g	g	g	g	g	g	g	<0.75
Blank A	0.4925	0.4926	0.0001	1.1548	1.1548	0.0000	0.1728	0.1734	0.0006	133.8218	133.6087	0.2131	Good
Blank B	0.5070	0.5071	0.0001	1.1588	1.1590	0.0002	0.1605	0.1606	0.0002	133.9320	133.4660	0.4660	Good
PE A	0.5002	0.5003	0.0001	1.1531	1.1532	0.0001	0.1622	0.1629	0.0007	134.7459	134.3408	0.4051	Good
PE B	0.4751	0.4753	0.0002	1.1638	1.1639	0.0001	0.1650	0.1652	0.0002	133.8457	132.6992	1.1465	Bad
ASFR6 A	0.4801	0.4802	0.0001	1.1642	1.1642	0.0000	0.2051	0.2063	0.0012	141.8007	141.2772	0.5235	Good
ASFR6 B	0.5039	0.5040	0.0001	1.1228	1.1229	0.0001	0.1688	0.1691	0.0003	142.0381	141.4987	0.5394	Good
Blue A	0.5165	0.5166	0.0001	1.1626	1.1628	0.0002	0.1715	0.1726	0.0011	134.4721	134.2397	0.2324	Good
Blue B	0.4766	0.4768	0.0002	1.1473	1.1473	0.0000	0.1871	0.1874	0.0003	134.5267	133.8301	0.6966	Good
DS2FR A	0.5074	0.5073	-0.0001	1.1581	1.1581	0.0000	0.1604	0.1607	0.0003	135.3081	134.6062	0.7019	Good
DS2FR B	0.5136	0.5137	0.0001	1.1288	1.1289	0.0001	0.1947	0.1948	0.0002	134.8276	132.9733	1.8543	Bad
BlackFR A	0.4761	0.4761	0.0000	1.1369	1.1368	-0.0001	0.1757	0.1760	0.0003	141.9277	141.3059	0.6218	Good
BlackFR B	0.4822	0.4822	0.0000	1.1670	1.1672	0.0002	0.1668	0.1672	0.0004	142.3480	141.8464	0.5016	Good

The last group of columns shows the initial weight of the entire jar configuration prior to and after testing, as well as the mass loss found by subtracting the final weight from the initial weight. This serves as a control and acts as a gauge for the tightness of the seal. A perfect seal would allow no mass loss for the entire system, and the resulting constant weight from a perfect seal from the beginning to the end of the testing procedure would confirm that that the entire system was contained within the jar with no losses. However, the jars in this experiment leaked, and it is suspected that the losses were mostly evaporated water. These losses mean that during testing, volatiles from the plastics could have evaporated and could have had less interaction with the coupons. Some of the jars were completely dry when they were opened, indicating that the test environment did not have 100% RH. It was decided that the jars which lost more than 0.75 g of mass would be considered to have a poor seal, and the data would be analyzed accordingly.

The mass gain table shows no detectable change in weight on coupons that can be ascribed to corrosion. However, this test method does not appear to be meaningful for coupons of this size in the test environments. The mass changes in copper and silver were beyond the detection limit of the scale, so the measurements are essentially meaningless. The mass gains in the lead coupons that were significant were not repeated, so the data does not give meaningful results.

Photographs of each metal coupon were taken immediately after removal from the sealed jars. These photographs have been compiled in Appendix A, where the corrosion spots are visible. A visual assessment was made and is shown on the following table, Table 6.2-2.

Table 6.2-2. Oddy Test observations of coupon condition immediately following testing

	Copper	Silver	Lead
Blank A	Minor discoloration - red tint along bottom of coupon	Marks	Marks
Blank B	Minor spotting	Streaks	Minor area of corrosion
PE A	Many spots; back side (inside of fold) discolored with a red/purple tint; blackened near bottom edge	Square shaped corrosion spot - might be from contamination prior to test and after cleaning procedure	White corrosion spot
PE B**	Black discoloration on bottom edge; black dots on front	Right half of front is slightly discolored/yellow	Streak of white
ASFR6 A	Back bottom edge has semi-circle of discoloration	Slightly spotty	Large area of white corrosion; Orange corrosion spot on outer fold
ASFR6 B	Black discoloration on bottom corner of both the front and back	Slightly spotty	Minor area of corrosion
Blue A	Black discoloration spot inside flap edge	Slightly spotty	Badly corroded; white markings on outside; orange corrosion spots around inside flap edge
Blue B	Black discoloration on bottom edge; green streak across front	Slightly spotty	Two white corrosion spots on each side
DS2FR A	Bad corrosion - Black discoloration on bottom edges; green discoloration along inside edge of flap	Slightly spotty	Front of coupon is coated
DS2FR B**	Slightly coated with discoloration	OK	OK
BlackFR A	Very bad corrosion; discoloration and blackened areas	Some discoloration	OK
BlackFR B	Black discoloration spots	Slightly spotty and discolored	Large area of white corrosion

**Not sealed

Visual assessments were also made by a variety of people who rated the coupons by filling out a chart, shown in Appendix B. The chart instructed the observer to rate the test coupons to on a scaled from 1-5, compared to freshly polished and cleaned coupons, where 1 represents the best condition, and 5 represents the worst condition. Ratings were to be made in reference to the overall corrosion, generally seen in color change, and in spots of corrosion, rated by the percentage of the total area covered by spots. The chart was broken into two columns, one for overall corrosion and one for spots. This seemed to be the best approach to ensure clear responses from the raters, and to control what they were focusing on as they rated each coupon. Due to the inconsistent nature of the results, shown in Appendix A-2, the data collected from this poll was not accepted as conclusive. This rating process is one of the methods used to rate Oddy test results, and is reflective of the truly subjective nature of this test [8].

6.2.2 Data Analysis

The Oddy test results are difficult to interpret because corrosion spots seemed to be inconsistent from sample to sample, and some corrosion or tarnishing was noted on the blanks and the coupons exposed to untreated polyethylene. It is likely that the majority of the corrosion is caused by oxidation from the ambient oxygen and elevated heat inside the Oddy test jars. Some versions of the test fill the test environment with N_2 in order to rule out the presence of oxygen; however, in a real-life setting, oxygen is going to be present. Although allowing the ambient oxygen to be present adds a variable to the test, it made the overall test more simplistic and imitated the normal Oddy test that would be performed in a museum laboratory.

The results from the poll were so scattered that they were statistically insignificant. It might be suggested that in order to make the polling procedure work better, an example of each level of corrosion might be present, even in photographic form, as a point of comparison. This is done in some versions of the Oddy test, but even so, the test remains extremely subjective. The corrosion spots on the coupons were later analyzed by XRF and XRD. These results provided more concrete evidence about the nature of the corrosion on each coupon and will be discussed below.

In general, the visible corrosion that occurred during the Oddy tests was no better or worse from the FR plastics than in the blank test samples and the pure polyethylene samples. Although the test itself fail in many respects, results do not suggest that any of the materials are highly corrosive.

6.3 Electrochemical Testing

6.3.1 Data Results

The electrochemical testing yielded a generous amount of data regarding the corrosive characteristics of the extracts on copper. The data collected was in the form of a polarization resistance measurement for each extraction. The Gamry software was used to calculate the corrosion rate in milli-inches per year (mpy), given the surface area, and standard values for properties of the metal. Although the corrosion rate is a more applicable value than the polarization resistance, the extra calculations may introduce some error. Therefore, it was decided to view the measured values on a comparative scale, i.e. relative to each other, and to water and nitric acid. Other materials were also tested that are known to be corrosive in the museum environment.

Table 6.3-1 shows the average corrosion rates and polarization resistance obtained from the testing. Figure 6.3-1 and Figure 6.3-2 show graphical representations of the clusters of polarization resistance data and corrosion rate data collected for each extraction. Note that the corrosion rate for the nitric acid has been removed because it is out of the range necessary to fit on the graph with the other data.

Table 6.3-1. Corrosion rate (CR) in units of milli-inches per year and polarization resistance (R_p) in units of k-Ohms.

	CR (mpy)		Rp (kOhms)	
Extraction	Average	StDev	Average	StDev
(1) Ultra DI H2O	0.54	0.13	77.01	18.46
(2) Tap Water	1.32	0.26	31.15	5.41
(3) Pure PE	0.83	0.09	48.68	6.10
(4) ASFR6	1.11	0.18	37.00	6.23
(5) DuraSkrim (DSFR)	1.20	0.22	34.18	5.50
(6) Blue Deck Cover	1.08	0.20	38.26	7.46
(7) Black FR	1.39	0.33	30.02	6.54
(8) ZnBr2	4.28	0.63	9.51	1.58
(9) Plywood	4.85	1.68	9.01	2.64
(10) Cellulose Acetate	5.61	0.92	7.29	1.33
(11) 1%HNO3	62.83	5.20	0.64	0.05

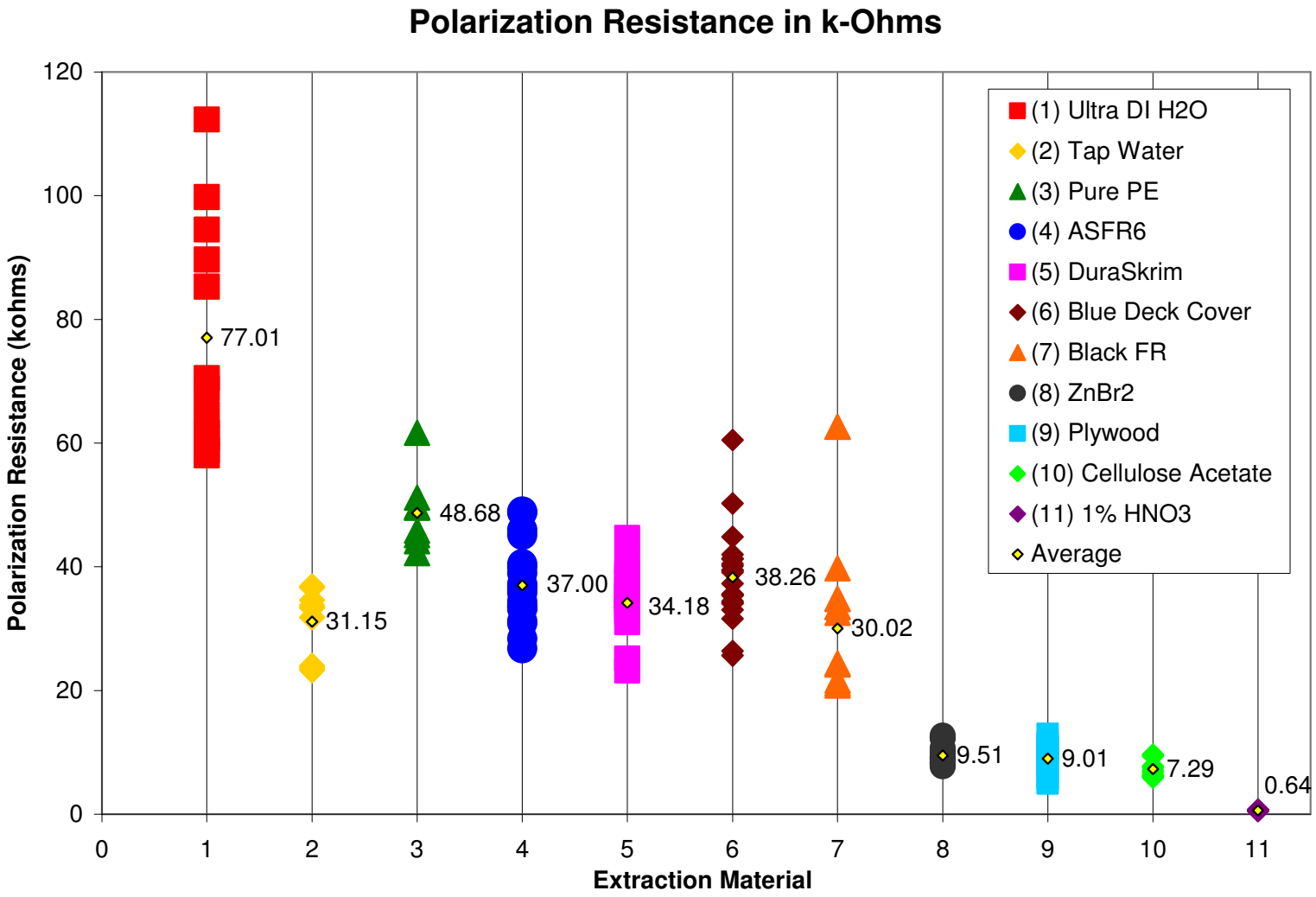


Figure 6.3-1. Polarization resistance data taken during electrochemical testing

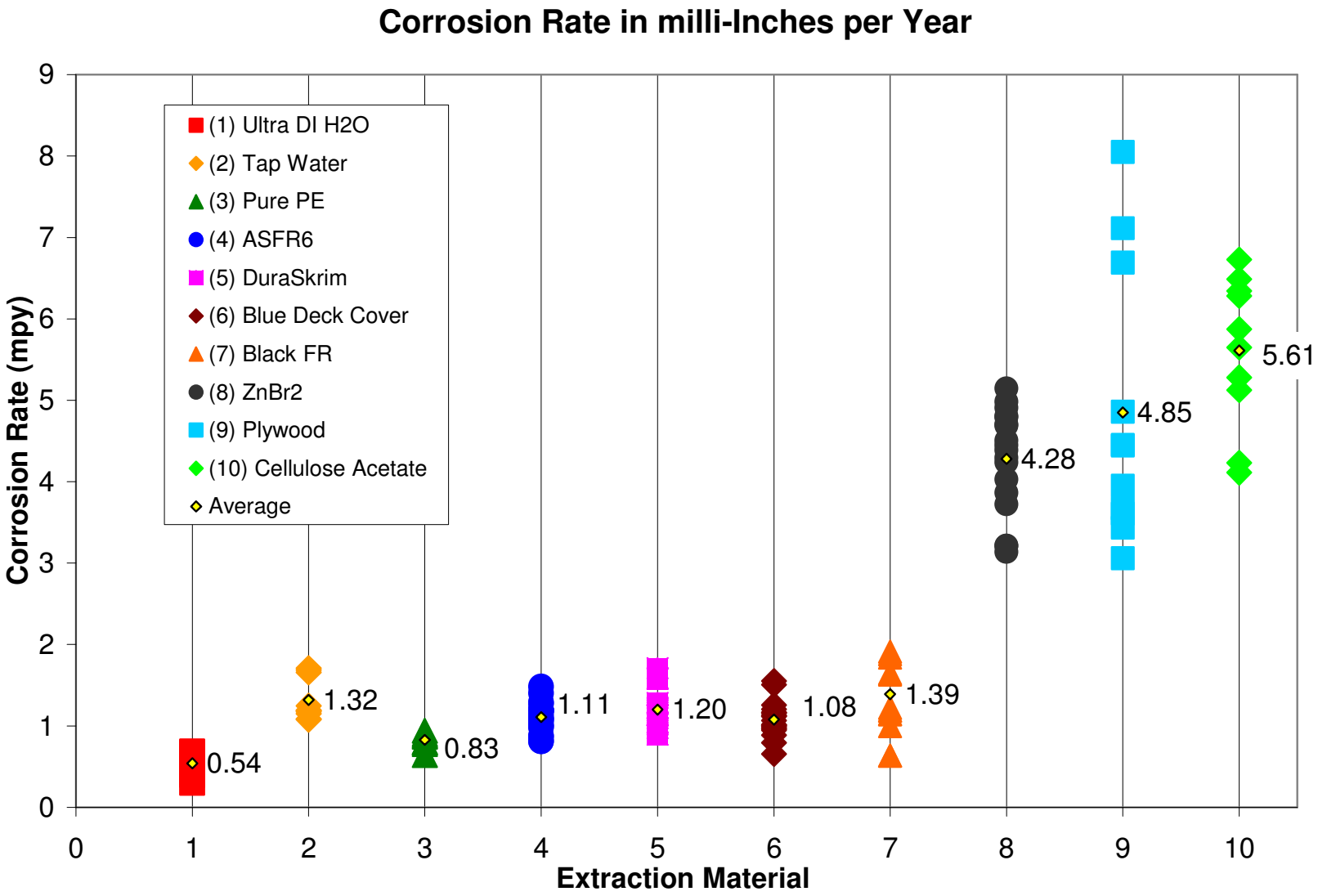


Figure 6.3-2. Corrosion rates measured from electrochemical tests

6.3.2 Data Analysis

The electrochemical testing results indicate that the procedure was effective in separating the data into a range of values. Because of the calculation to convert polarization resistance to corrosion rate, derived from Equation 4.2-4 and Equation 4.2-6, the R_p and the CR values are inversely related. As mentioned earlier, it is not necessarily safe to trust the corrosion rate values; however, the data can be used comparatively. Looking at Figure 6.3-2, the average corrosion rate of Ultra-DI water was found to be 0.54 mpy, while the 1% nitric acid had an average corrosion rate of 62.8 mpy, which makes sense in terms of corrosivity

Because nitric acid is so corrosive compared to the extracts, the data is shown normalized to methanol or ultra-DI water, as can be seen in Table 6.3-2. Tap water was found to have similar corrosivity to copper as all the FR plastic extracts.

Table 6.3-2. Normalized data excluding nitric acid.

	Normalized Data			
Extraction	CR	CR %	Rp	Rp %
(1) Ultra DI H2O	0.00	0.00	1.00	100.00
(2) Tap Water	0.15	15.38	0.34	34.22
(3) Pure PE	0.06	5.72	0.59	59.37
(4) ASFR6	0.11	11.24	0.43	42.61
(5) DuraSkrim	0.13	13.02	0.39	38.57
(6) Blue Deck Cover	0.11	10.65	0.44	44.42
(7) Black FR	0.17	16.77	0.33	32.60
(8) ZnBr2	0.74	73.77	0.03	3.18
(9) Plywood	0.85	85.01	0.02	2.47
(10) Cellulose Acetate	1.00	100.00	0.00	0.00

In addition, the data for other materials tested, in Table 6.3-1, indicate that the results follow what would be expected. Wood and cellulose acetate are known to be damaging to metals and are avoided for museum uses. The $ZnBr_2$ was formulated to

have 6% bromine in the solution. This was meant to represent a normal amount of bromine found in brominated FR plastics; however, the bromine ions are more easily liberated in this solution, compared to extracts from the plastics. This shows that bromide species are definitely corrosive in high concentration, although the reactions that take place in this cell are not certain.

Pure polyethylene (PE) is the second lowest in terms of corrosion rate, as expected. Pure PE is trusted by conservation scientists and curators, apparently for good reason. Although slightly higher than corrosion rates were obtained for the FR plastics, all did well in comparison to the known corrosive agents (plywood, cellulose acetate and nitric acid). In fact, it may be stated that they are about as corrosive as tap water to copper metal. These test results provide a first step toward showing that FR plastics can be used in museum applications, including applications involving metals.

6.3.3 Statistical Analysis

In order to determine if the data collected is statistically different, a t-test can be used. In doing a t-test, it is possible to see if the FR plastics gave corrosion rates that are statistically different than those of pure PE. When looking at the difference between the values, it is easy to see that the FR plastic corrosion rates seem to cluster apart from the pure PE, but it is more important to judge the difference by assessing the mean values relative to the variability of the measured corrosion rates.

$$t-value = \frac{Signal}{Noise} = \frac{\overline{X}_{FR} - \overline{X}_{PE}}{SE(\overline{X}_{FR} - \overline{X}_{PE})}$$

Equation 6.3-1. T-value for the t-test.

The bottom of this equation is known as the standard error of the difference, and is shown in Equation 6.3-2., where variance is taken to be the standard deviation squared.

$$SE(\overline{X}_{FR} - \overline{X}_{PE}) = \sqrt{\frac{\text{var}_{FR}}{n_{FR}} + \frac{\text{var}_{PE}}{n_{PE}}}$$

Equation 6.3-2. Standard error of difference.

The computed t-value is then compared to the values found in a standard table of significant values. To do this, the degree of freedom (df) needs to be determined, shown in Equation 6.3-3, and a risk level (alpha level) needs to be assigned. In this case, the t-values will be evaluated at an alpha level of 0.05, meaning that 5% of the time, a statistically significant difference between the means would be found, even if there was none.

$$df = n_{FR} + n_{PE} - 2$$

Equation 6.3-3. Degrees of freedom.

The analysis was done using pure PE as the control measurement. Assuming the PE is a safe plastic to be used in a museum, the FR plastics and other materials tested can be compared to it as a reference point. Table 6.3-3 shows all the values, and shows that each measurement taken is statistically significant in comparison to the corrosion rates of pure polyethylene, because the standard t-values were lower than the calculated t-values, indicating that the t-values were all large enough to be significant.

Table 6.3-3. Statistical analysis of t-value to determine statistically significant differences between pure PE and other measured corrosion rates in milli-inches per year (mpy).

Extraction	Average	StDev	Variance	n	Calculated t-value	df	t-value α=0.05	Statistical Difference?
(1) Ultra DI H_2O	0.54	0.13	0.02	12	-5.89	18	1.734	yes
(2) Tap Water	1.32	0.26	0.07	10	5.56	16	1.746	yes
(3) Pure PE	0.83	0.09	0.01	8	–	14	1.761	–
(4) ASFR6	1.11	0.18	0.03	21	5.54	27	1.314	yes
(5) DuraSkrim	1.20	0.22	0.05	18	6.08	24	1.711	yes
(6) Blue Deck Cover	1.08	0.20	0.04	22	4.70	28	1.701	yes
(7) Black FR	1.39	0.33	0.11	13	5.78	19	1.729	yes
(8) $ZnBr_2$	4.28	0.63	0.40	18	22.72	24	1.711	yes
(9) Plywood	4.85	1.68	2.82	11	7.92	17	1.740	yes
(10) Cellulose Acetate	5.61	0.92	0.85	10	16.33	16	1.746	yes
(11) 1%HNO_3	62.83	5.20	27.04	15	46.16	21	1.721	yes

6.4 XRF of Plastic Sheets, Extracts & Corrosion Spots on Oddy Coupons

6.4.1 Data Results

The elemental composition of each of the plastic sheets was investigated using XRF analysis. Table 3.1-1 shows the elements that were detected in each plastic.

Table 6.4-1. Elements detected by XRF in the plastics samples.

Sample	Elements Detected
Pure polyethylene sheeting (from Freer Gallery of Art)	None
Black	Br (major), Sb (major), Ni (minor); P and S possible in trace amounts
Blue (Blue Deck Cover)	Br (major), Sb (major), Ni (minor)
White (ASFR 6)	Br (major), Sb (major), Ni (minor), Ti (minor)
Clear-white with fibers (DSFR)	Br (major), Sb (major), Ni (minor), Ti (trace)

Besides the solid plastics, the liquid extracts made from the plastics used for electrochemical testing were also examined by XRF. The liquids were examined in Kapton window cups using a Cu-Ti-Al filter at 40 kV and 3 μA for optimal sensitivity to bromine (Br) and antimony (Sb). However, no elementals were detected in the extracts.

Some of the coupons, which had been used in the Oddy tests, including copper, silver, and lead, and which showed visible signs of corrosion, were also examined by XRF. The area of examination in these cases focused on visibly oxidized or corroded spots on some coupons, although this was inexact and included un-corroded areas. No elements, other than the metals, were detected. However, it must be noted that examination of Pb was hampered by interference of the Pb lines with both Br and S. Some of the metal coupons, including copper and silver, which had been exposed to

corrosive conditions in the electrochemical tests were also examined by XRF. No elements were detected on these coupons either.

6.4.2 Data Analysis

The results from the XRF testing of the plastic sheets confirmed that the flame retardant (FR) plastics, including the Black, Blue, ASFR6, and DSFR, are heavily brominated as expected. The bromine is most likely in the form of poly-brominated diphenyl ether compounds. The FR plastics additionally contain antimony (Sb), most likely in the form of SbO or Sb_2O_3, which are also common ingredients in fire-retardant formulations for synergistic fire retarding mechanism. The presence of nickel (Ni) was not expected and its nature is unknown. The presence of titanium (Ti) in two of the plastics indicates the presence of TiO2, which is a common white pigment added to materials. The presence of sulfur (S) and/or phosphorus (P) in the black plastic was not confirmed.

While XRF analysis indicated that there were significant amounts of bromides in the FR plastics, it is interesting that bromine has was not detected in the extracts or on the exposed metals, although bromide species are suspected to be volatile and corrosive agents. However, it should be noted that the presence of bromine in these tests may have been below the limits of detection of this instrumental technique. Overall, the results do appear to correlate with the low corrosion rates obtained for Cu in the electrochemical tests, but negative results are not strong evidence or confirmation that BFRs are truly safe for use in museums.

6.5 XRD of Coupons & Extractions

6.5.1 Data Results

XRD was conducted on select metal coupons which had been exposed to the different plastics in the Oddy test. This analysis served as a more scientific approach to evaluating the Oddy test results. The results from these tests are shown in diffraction patterns which reveal the identity of crystalline structures that are present in the tested material. This data is summarized in Table 6.5-1 and the actual diffraction patterns are shown in Appendix A.2.

Table 6.5-1. Sample descriptions from Oddy test coupons with estimated quantities of molecular structures found with XRD analysis (from Smithsonian Institution Museum Conservation Institute internal report).

Sample Type	Sample description	Identified Phases	Estimated Quantity	PDF #
1	Blue A - Pb corrosion: brown, shiny, plate-like crystals	Litharge (PbO)	Major	01-085-1739
		Plumbonacrite ($Pb_5(CO_3)_3O(OH)_2$)	Major	99-000-2978
		Lead Oxide Carbonate Hydroxide	Major	00-019-0680
		Lead Carbonate Hydroxide Hydrate	Major	00-009-0356
2	PE A - Pb corrosion: brown, shiny, plate-like crystals	Lead	Major	03-065-2873
		PbO	Major	03-065-2809; 01-085-1739
		Plumbonacrite	Major	99-000-2978
		Lead Oxide Carbonate Hydroxide	Major	00-019-0680
3	DSFR A - Pb corrosion: spots, pale and greyish	Lead	Major	03-065-2873
		PbO	Major	01-085-1739; 00-052-0772
		Plumbonacrite	Major	99-000-2978
		Lead Oxide Carbonate Hydroxide	Major	00-019-0680
4	Blue A - Cu corrosion: black-grey spots from outside of coupon	Copper	Major	01-070-3039
		Tenorite (CuO)	Major	00-048-1548
5	DSFR A - Cu corrosion: black-grey spots from outside of coupon	Copper	Major	01-070-3039
		Tenorite (CuO)	Major	00-048-1548
6	DSFR A - Ag corrosion: spots on metal coupon, pale and grayish	Silver	Major	01-087-0719
		Copper	Major	98-000-0034
		(?) Bromargyrite (AgBr)	Possible, but trace	01-079-0148

6.5.2 Data Analysis

The XRD analysis of the selected metal coupons and their visible corrosion products after exposure in the Oddy Tests did not provide evidence of reaction with any of the FR plastics, except possibly in the case of the silver exposed to DSFR. The lead coupons, which in several instances showed the formation of orange-colored crystals, proved to have formed lead oxides and carbonates. It is likely that this occurred from exposure to heat and humidity, and not from any volatiles emitted from the plastics. This same type of corrosion was found on samples from two of the FR plastics, as well as the pure polyethylene sheeting, further adding to the evidence that the corrosion which formed was not related to the chemical additives found in the FR materials.

In the case of copper, several coupons exhibited grey and black spots after the Oddy test exposures. These spots were identified by XRD as tenorite, the cupric oxide. This oxidation product tends to form with high heat, and therefore may be ascribed to the temperature used in the testing protocol rather than any volatiles emitted from the plastics.

In the case of silver coupons, most coupons appeared rather unchanged after testing. Small grayish spots were too thin to be sampled by XRD. However, direct examination of coupons was possible because pattern lines from expected corrosion products generally do not interfere with lines from the metal alloy (in this case a silver-copper alloy similar in composition to sterling silver). Very small irregularities in the pattern obtained from the coupon exposed to DSFR plastic could in this case be interpreted as possible evidence for the formation of AgBr. However, this evidence is

slight and inconclusive. Furthermore, this evidence was not supported by XRF analysis, as discussed earlier.

6.6 pH of Extractions

6.6.1 Data Results

The following pH measurements, shown in Table 6.6-1, were obtained for each of the 11 extracts tested in the electrochemical tests, in order to see if the acidity of the solutions correlated to the measured rates of corrosion and polarization resistances.

Table 6.6-1. pH measurements of each extraction.

Extraction	pH
(1) Ultra DI H2O	5.5
(2) Tap Water	7.0
(3) Pure PE	7.3
(4) ASFR6	7.2
(5) DuraSkrim	7.0
(6) Blue Deck Cover	6.9
(7) Black FR	7.0
(8) ZnBr2	5.3
(9) Plywood	5.5
(10) Cellulose Acetate	5.2
(11) 1%HNO3	0.8

6.6.2 Data Analysis

In order to determine if any correlation between pH and corrosion rate existed, the measured corrosion rates and polarization resistances are plotted as a function of the measured pH values in Figure 6.6-1 and Figure 6.6-2. Average values are used for the polarization resistance (R_p) and the corrosion rate (CR) values were used.

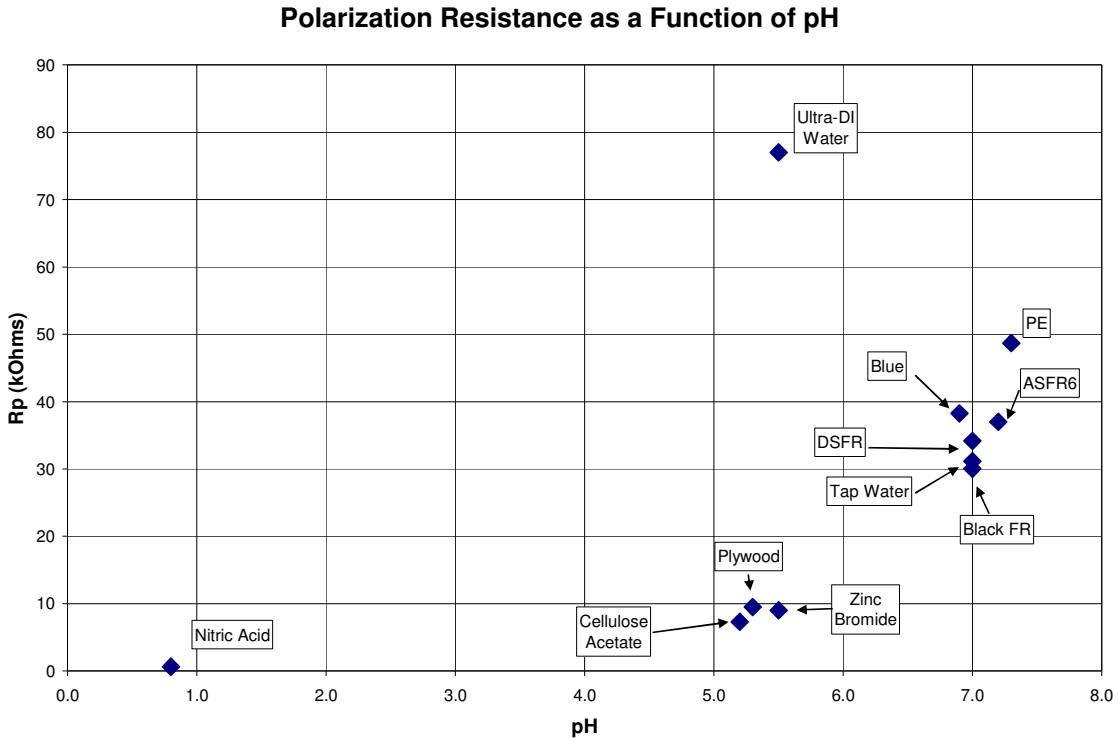


Figure 6.6-1. Polarization resistance (R_p) as a function of pH.

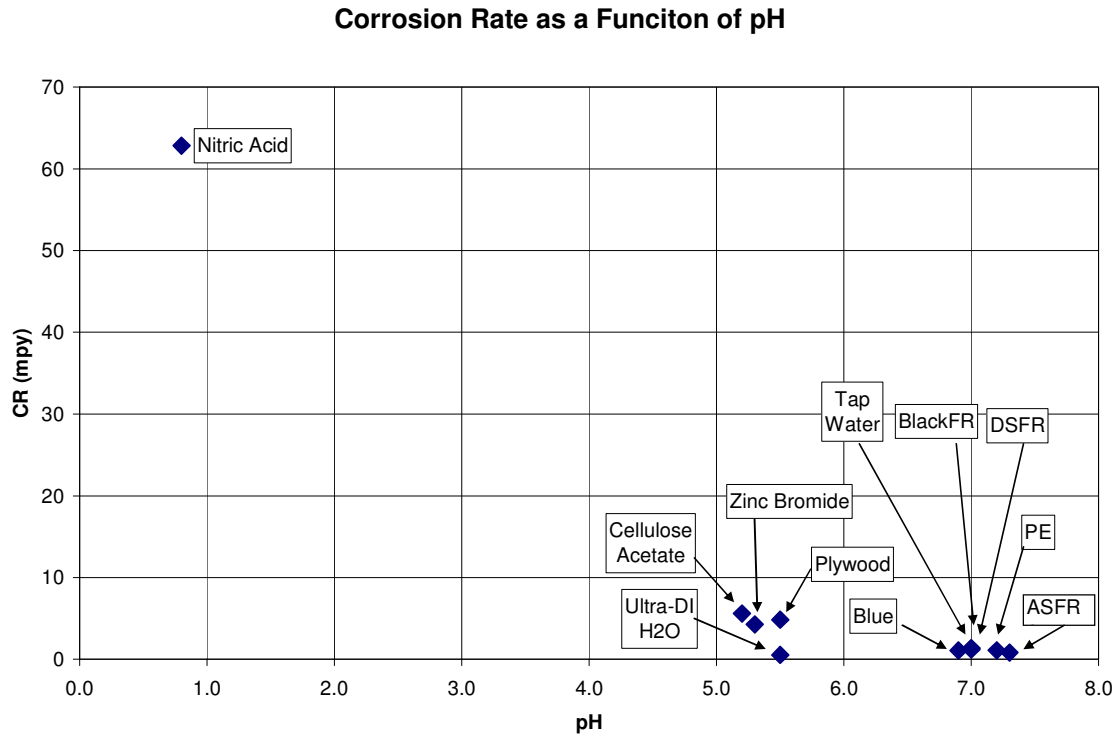


Figure 6.6-2. Corrosion rate (CR) as a function of pH.

It would be expected that a neutral pH (around 7.0) would be the least corrosive and have the lowest corrosion rate. This appears to be true for the cluster of pH measurements around 7.0 with low corrosion rates and high polarization resistances. It is interesting to note that the ultra-DI water has a lower pH than the extracted plastic liquids. This is likely due to the formation of carbonic acid in water from dissolved carbon dioxide from the atmosphere. However, it is interesting that the extracts, made with the same ultra-DI water, did not experience this phenomenon. It should also be noted that the lower pH of ultra-DI water does not appear to translate into higher corrosion rate, although measurements here in this case are hampered by low conductivity. As expected, the nitric acid had a very low pH and very high corrosion rates and very low polarization resistance measurements. It is suggested by these results that there is a direct relationship between pH and corrosion rate for the different solutions.

Materials that are known to corrosive in museum environments, including cellulose acetate and plywood, had slightly lower pH values meaning they were more acidic, and slightly higher corrosion rates than the extracts. Although the pH and corrosion rates values were all fairly close, there were obvious differences between the known corrosive materials and the plastic extracts. Perhaps by using pH tests and the electrochemical corrosion tests in conjunction, a more complete understanding of the corrosivity of a certain material can be assessed. These results seem to again suggest that the FR plastics studied do not cause their surrounding environment to become acidic and in the presence of humidity, are not particularly corrosive to metals in museums.

Chapter 7 Conservation Risk Assessments

7.1 Identification of Risks to Collections

7.1.1 Agents of Deterioration and Types of Risk

Waller identifies the ten agents of deterioration as physical force, fire, water, criminals, pests, pollutants, light and radiation, incorrect temperature, incorrect relative humidity and custodial neglect [13]. Within the categories of the agents of deterioration, many risks can be identified. A chart used by Waller to organize the risks by their agent of deterioration, categorize the type of risk, and identify levels for control is shown in Appendix B, figure B-2. To assign a "type" value to each risk, frequency of occurrence and the severity of the effect are assessed, as depicted in Figure 7.1-1.

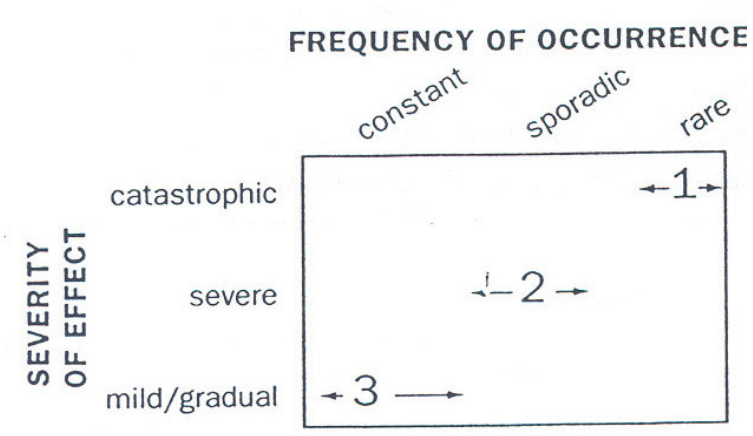


Figure 7.1-1. "Ranges of frequency and severity of the types of risk [13]."

7.1.2 Identifying the Risks

According to Waller's model, in the assessment of the risks associated with fire and the use of FR plastics in museums, the major agents of deterioration are Fire and

Pollutants. Figure 7.1-2 shows these agents of deterioration, and the different examples of the risks associated with them.

Agent of Deterioration	Type of Risk	Example of Risk
Fire	1	Fire with flashover to other objects which would possibly flashover in other fire compartments (total losses)
	2	Smoke damage from fire
	2	Flame causing damage or loss to building, objects
Pollutants	3	Corrosive off-gassing from FR plastics

Figure 7.1-2. Identified agents of deterioration for the use or non-use of FR plastics in museums.

7.2 Assessing Magnitudes of Risk

7.2.1 Fire

The calculated magnitude of risk is the product of probability and severity, as shown in Figure 7.2-1, as shown in Chapter 2.

Magnitude of Risk = Probability (or extent) x Severity

(Severity = Fraction susceptible x Loss in value)

Magnitude of Risk = Probability (or extent) x Fraction susceptible x Loss in value

Figure 7.2-1. Magnitude calculations [13].

For the sake of simplicity, and a lack of data, the fire risks will be analyzed graphically, using statistical data where available. According to NFPA 909 statistics, there was an average of 86 museum fires reported per year from 1980-1998 [11]. This number may be rounded up to 100 fires because many fires go unreported. According to

the American Association of museums, there are approximately 17,500 museums in the U.S. [50]. This implies that the probability of a museum fire occurring is 0.0057.

$$p = \frac{100\,fires\,/\,year}{17{,}500 museums} = 0.0057$$

Equation 7.2-1. Probability of a fire occurring in a museum each year.

According to NFPA, the average total loss per year for the 86 fires is approximately $1.9 million, so the average loss per fire is $22,000 [11].

$$LV = \frac{\$1{,}900{,}000}{86\,fires} \approx \$22{,}000\,/\,fire$$

Equation 7.2-2. Average loss per fire.

The Fraction Susceptible (FS) is interpreted as "the part of the collection that is potentially subject to loss or damage by exposure to the risk being considered [1]." It is possible that an entire collection could be destroyed by a single fire if all objects of that collection were stored in a single location, and in this case, the FS would be 100%. Rather than estimating a value for the fraction of a collection that could be damaged in the case of a fire, the data will be plotted using the FS as an independent variable while the Magnitude of Risk will be the dependent variable, using the equation below.

$$\text{Magnitude of Risk} = 0.0057 \times FS \times 22{,}000$$

Equation 7.2-3. Calculated Magnitude of Risk for fire in a museum per year.

It is impossible to say exactly how much the use of FR plastics in lieu of regular, non-FR plastics will affect fire statistics. If statistics were available that looked at the first item ignited, and plastic sheeting were included, then more a definitive approach could be established. For the purposes of this study, it is assumed that flame retardant polyethylene sheeting will not be the first item ignited, based on the results of burn tests, which showed the difficulty to ignite the FR plastics with small heat sources. Because

roughly 9% of fires start during renovations from open flame, ember or torch (per NFPA 909), it is assumed that there will be plastic present, and that the probability of a fire occurring in these situations might be reduced to 6%. This would mean that the overall number of fires occurring per year would be lowered by 3%.

It might also be estimated that the 30% of fires that start from electrical distribution equipment might be reduced to 29% if FR plastics are used instead of untreated polyethylene. This reduction would imply that the number of fires occurring per year would be reduced by another 1%, totaling a 4% estimated improvement in the probability of fire occurring in a museum. Equation 7.2-4 shows the equation for Magnitude of Risk with this improvement in probability.

$$\text{Magnitude of Risk} = [0.0057 \times (1 - 0.04)] \times FS \times 22{,}000$$

Equation 7.2-4. Magnitude of risk reduced by 4% for the use of FR plastics.

The two scenarios are graphically compared, using the fraction susceptible (FS) as the independent variable, shown in Figure 7.2-2. This graph shows the difference that the 4% reduction, from the use of FR plastics, would make in the overall magnitude of risk of fire in a museum.

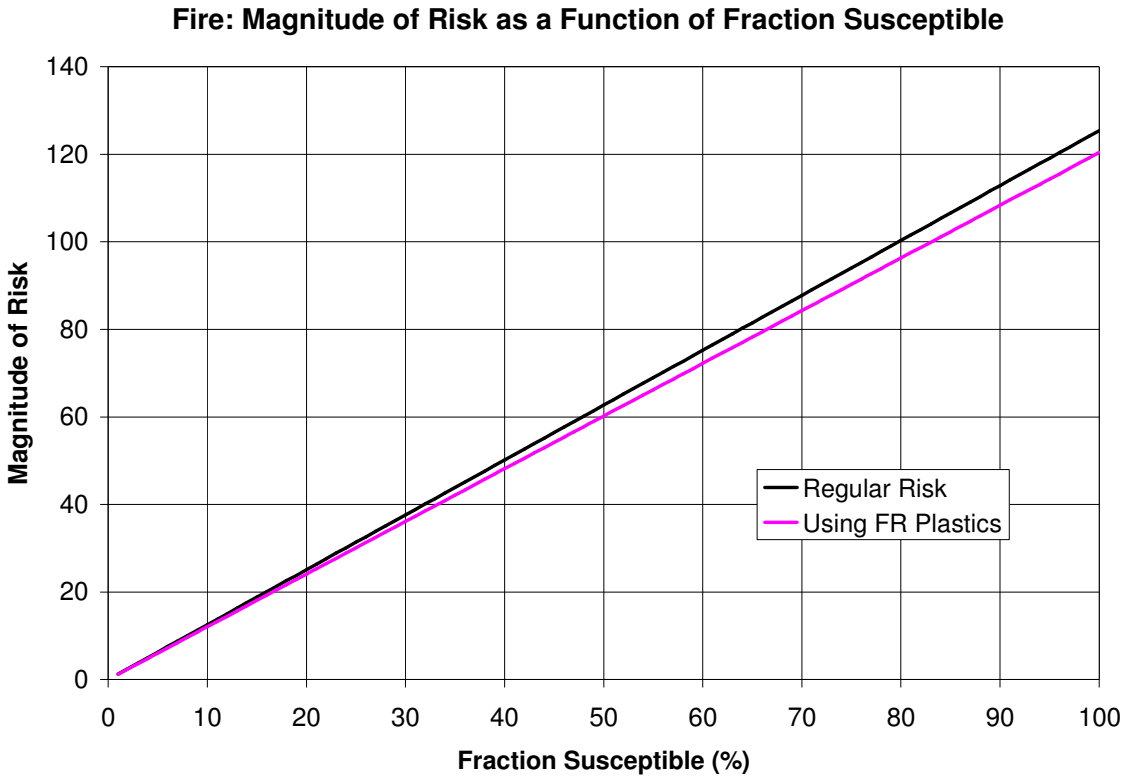


Figure 7.2-2. The magnitude of risk as a function of the FS value.

This shows that there is a small gain if a 4% reduction in the probability is all that is achieved by using FR plastics.

7.2.2 Contamination

Instead of using a probability, Waller suggests that for a type 3 risk for contamination, such as with the flame retardant polyethylene, it is better to use a measure of extent. Because the electrochemical tests allow the calculation of corrosion rate in mill-inches per year, these values can be used to estimate the Magnitude of Risk for using the FR plastics versus using pure PE. According to the results measured in Chapter 6, an average corrosion rate of 0.83 mpy will be assigned to pure PE, and so on for each of the other plastics, depending on their average corrosion rates.

The Fraction Susceptible (FS) will again be used as an independent variable. The Loss in Value (LV) will be estimated as $100,000 per inch of corrosion. This is an extremely rough estimate, and variation of the LV estimate could change the magnitudes of risk dramatically, but it will act as a filler value for these calculations.

$$\text{Magnitude of Risk} = 0.83 \frac{\text{milli-inch}}{\text{year}} \times 10^{-3} \frac{\text{inch}}{\text{mill-inch}} \times FS \times 100{,}000 \, {}^{\$}\!/_{\text{inch}}$$

Equation 7.2-5. Magnitude of Risk calculated for corrosion using pure PE.

The relationships between the different plastics using the FS as the independent variable are shown in Figure 7.2-3. The magnitudes of risk for the FR plastics are only slightly higher than the pure PE. Because this generic approach to the calculation of the Magnitude of Risk uses the same values for each plastic with the exception of the corrosion rate, it may be easier to simply compare corrosion rates. These are the values that will be of most serious concern to a conservator or conservation, and the Loss Values may be so high that no corrosion will be tolerated.

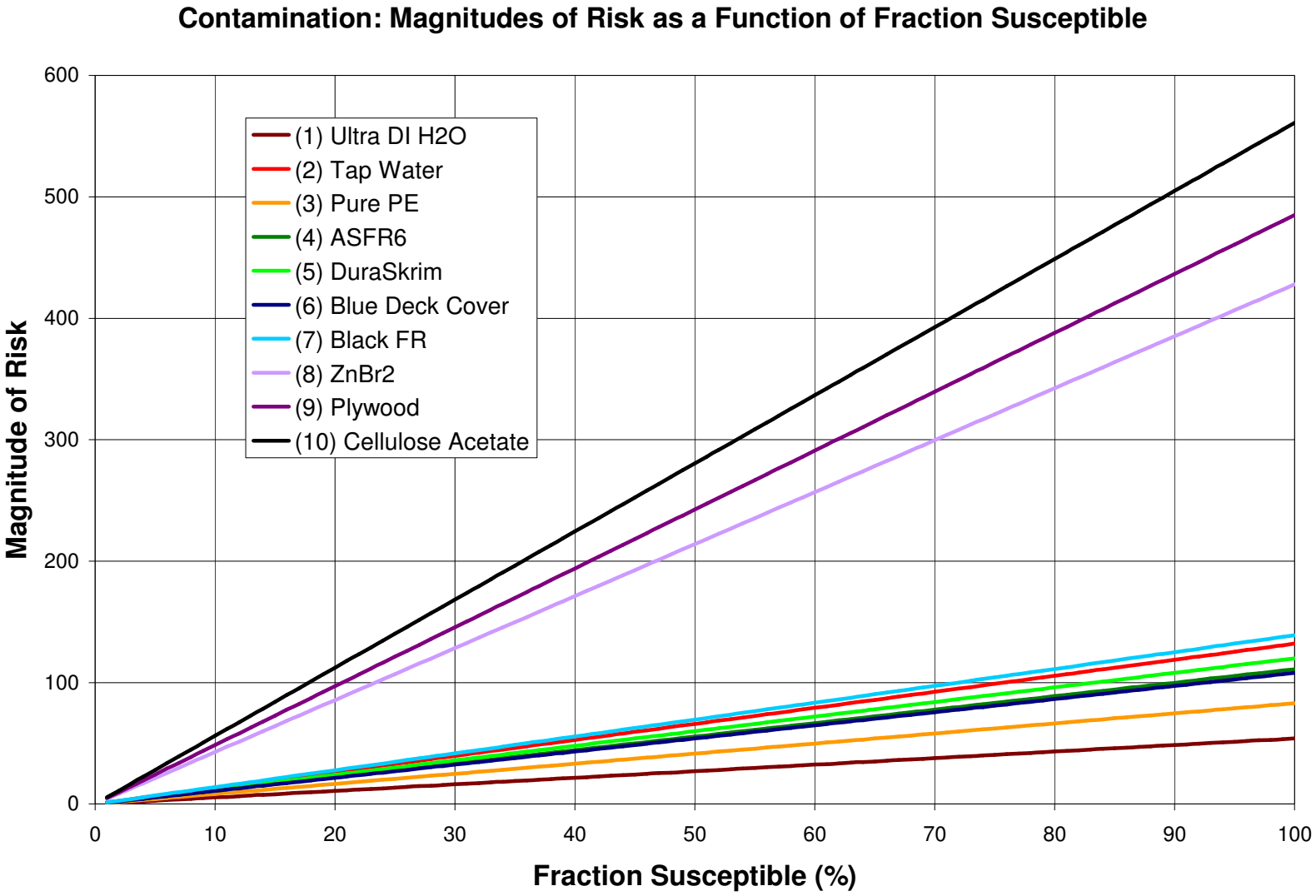


Figure 7.2-3. The magnitudes of risk for the contaminants, as a function of FS.

Another way to analyze this magnitude of risk would be to hold the Fraction Susceptible (FS) constant, and to look at a range of losses in value (LV). An estimate of 10% as the Fraction Susceptible to damage will be assumed; this means that in the event of contamination by corrosive plastics, 10% of the collection will suffer damages.

$$\text{Magnitude of Risk} = 0.83 \frac{\text{milli-inch}}{\text{year}} \times 10^{-3} \frac{\text{inch}}{\text{mill-inch}} \times 0.10 \times LV \, {}^{\$}\!/_{\text{inch}}$$

Equation 7.2-6. of risk for PE assuming FS=0.10.

The assumption of a 10% fraction susceptible is does not represent any real-life situation, but this is a good way to look at how the different values compare. Assessing the loss value in terms of dollar value per inch of corrosion is also an overly simplified approach, but the actual museum conditions, and the artifacts in question will dictate how these aspects are addressed. The ranges of the different plastics are shown in Figure 7.2-4.

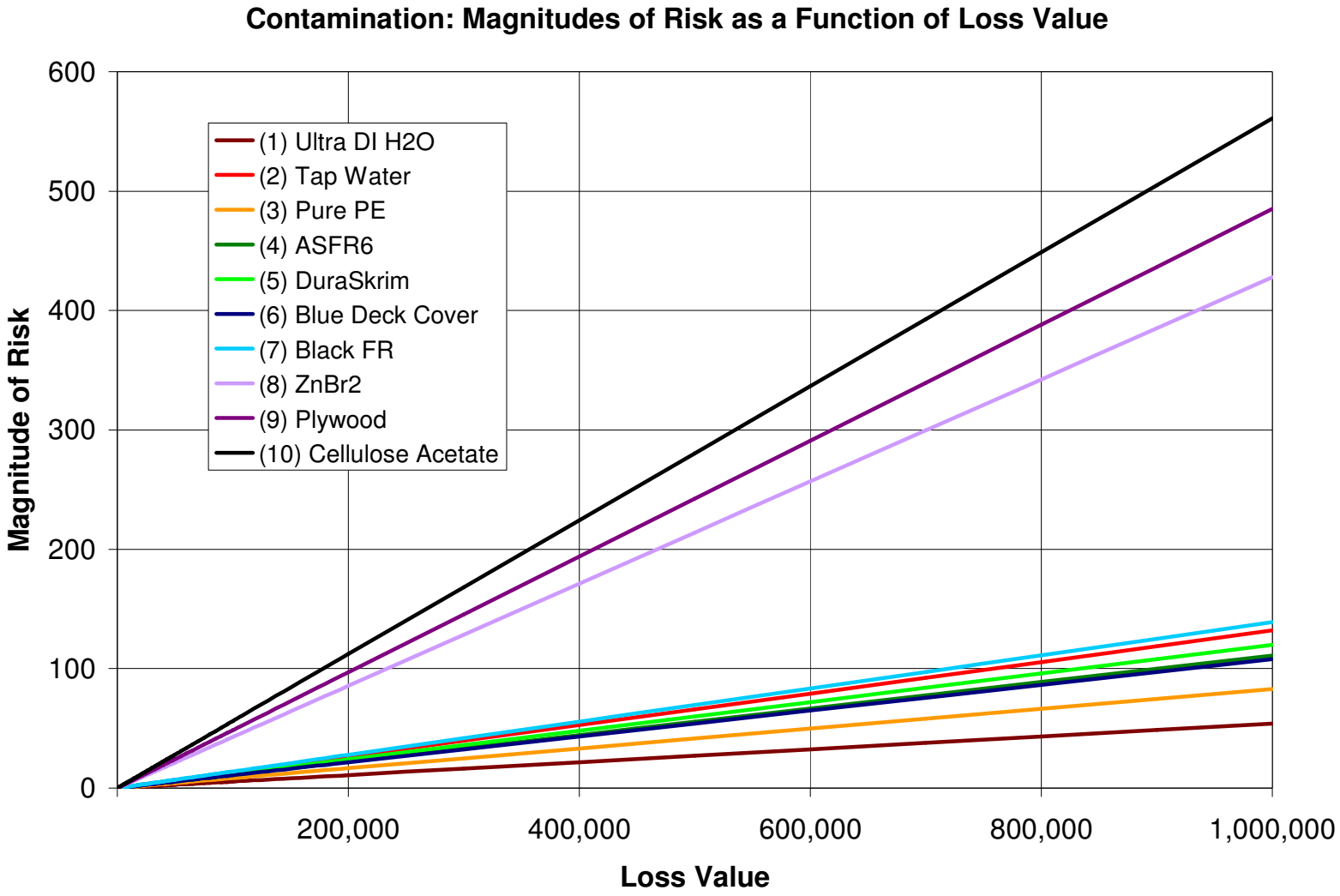


Figure 7.2-4. Magnitudes of risk for the contaminants, as a function of LV.

7.3 Identifying Possible Mitigation Strategies

Using flame retardant plastics is a mitigation strategy for reducing easily ignitable fuels in museum spaces. The best mitigation strategy for using the FR plastics would to first do careful in-house assessments (i.e., the Oddy test or Electrochemical testing if available) of the museum artifacts, including non-metal objects, in the area and how they might be affected by the plastics. It would also be wise to pay attention to any plastics that go unused for long periods of time because they can degrade as they age. Plastics should not be stored near UV light, as this tends to break plastics down much faster, which might cause the plastic to start to release damaging chemicals into the ambient atmosphere at an elevated rate.

If FR plastics are considered to be too risky for a collection, the best mitigation strategy to protect against contaminants would simply be to reject the use of FR plastics in that space. Of course, then the risk of fire will increase slightly, so to mitigate this risk, the non-FR plastics must be strictly limited in areas where they might be exposed to open flame or heat sources (as may occur during renovations). The non-FR plastics would be better suited for facilities that have automatic sprinkler systems, because this would reduce the risk for fire.

Controlling the use of plastics, both flame retardant and non-flame retardant, would fall under the policy and procedure levels of control. A museum's policy might insist on the use of FR plastics whenever possible, or it might insist that they be avoided whenever possible depending on how they assess the plastics. If anything, policy must be implemented insisting on the use of FR-plastics during renovations. Because of the limited exposure period, no corrosion damage should be expected, and the chances of

unwanted ignition and spread of fire will be reduced. Procedures can be implemented that require all new materials that will be exposed to at-risk collections to first undergo testing to ensure that they will not cause long- or short-term damage.

7.4 Cost, Benefits and Difficulties

If museums are forced to use FR plastics, the risk of ignition and spread of is reduced slightly. The calculations performed earlier represent rough estimates of magnitudes of risk, and depending upon the specific circumstances of the museum, the input values to the equations can fluctuate a great deal. By comparing the two situations as functions of the Fraction Susceptible, it is possible to see how they compare. However, it should be noted that the LV used for the contamination was based on $100,000 per milli-inch of corrosion, which is not a representative value. At using this LV input, the Magnitudes of Risk for fire, with or without FR plastics, are right in the midst of the contamination from FR plastics. This graph does not give much valid information, but this type of comparison can be used if a representative Loss Value can be assigned to the risk from contaminants. As mentioned, these calculations must be done with for a specific collection where the input values can be accurately estimated.

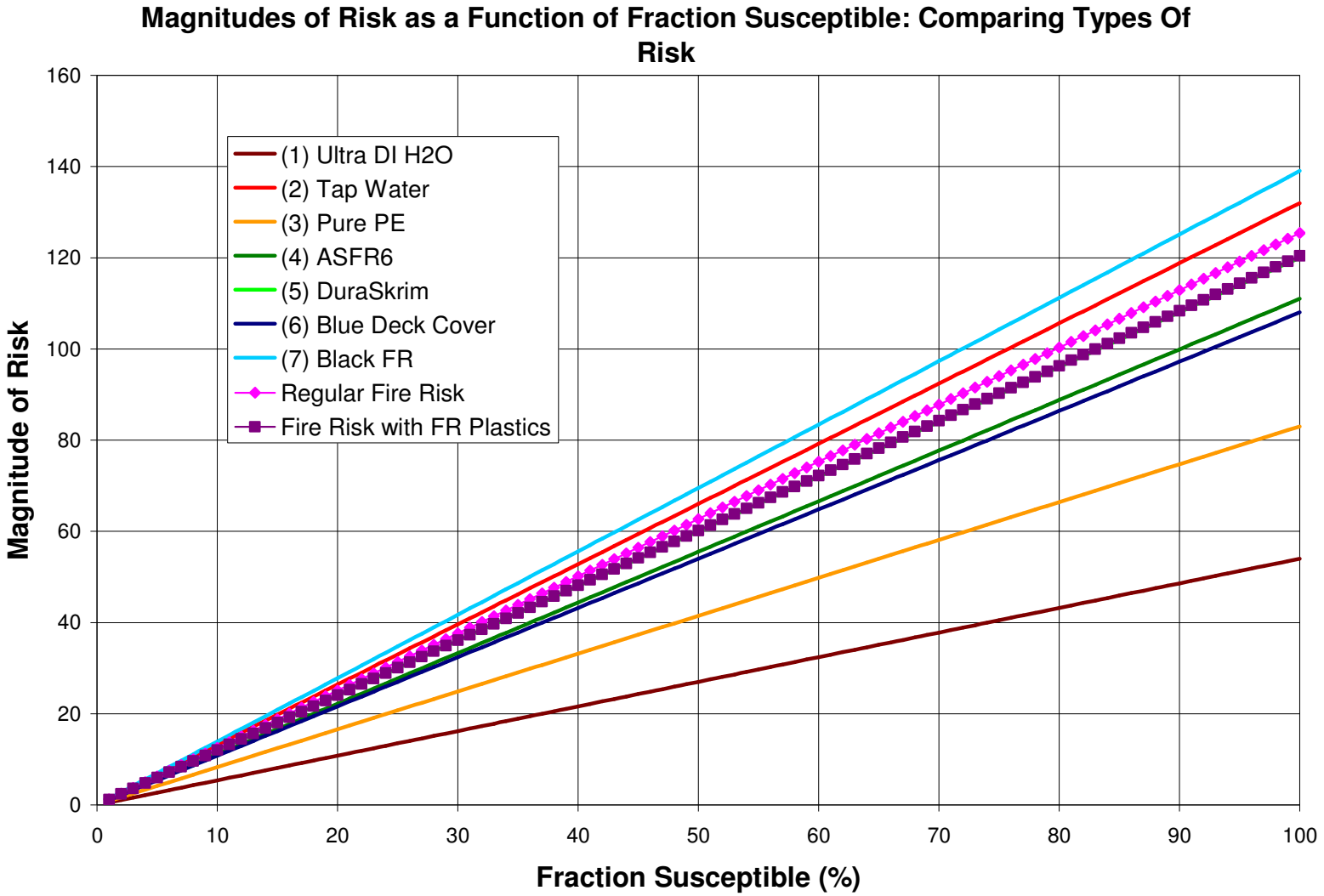


Figure 7.4-1. Comparing the magnitude of risks between risk of contaminants and risk of fire

If museums forgo the use of FR plastics and continue to use only pure polyethylen, they risk an increased load of easily ignitable materials. Although FR and non-FR plastics increase the fuel load, it is more difficult to ignite the FR plastics, and their use may help to slow the spread of fire. The actual risk of fire in a museum is low; however, the probability that the plastics will play any part in the fire is lower still. Therefore, equipping a museum with automatic sprinklers may be a more cost-effective approach given the statistics and estimated values in this assessment.

Finally, in regard to human health and the studies that declare polybrominated diphenyl ethers to be hazardous to the environment, it may be a bad decision to continue the use of these potentially harmful materials. A visit to a museum that uses FR plastics will not harm humans directly – it is the waste that is accrued from the use of the brominated plastics that will add to the growing problem with these chemicals in nature.

7.5 Risk Assessment Conclusions

Although the assessments performed here are too general to apply to specific situations, this methodology of risk assessment can be tailored to any museum scenario. With a specific exhibit or storage area in mind, the situation becomes more definitive and important details can be used to estimate the Loss Value, Probability, and Fraction Susceptible input values.

Although the Magnitude of Risk associated with the use of FR plastics has been shown to be greater than the Magnitude of Risk associated with the use of pure polyethylene and the Magnitude of Risk for fire without the use of FR plastics, they still might be useful in some museum or library settings. The corrosion rates of the FR plastics are statistically different from the corrosion rates for pure PE, but the FR values

are still below experimental corrosion rates obtained for known dangers such as plywood and cellulose acetate. Since the plastics will be used in milder conditions than those created in the tests, the benefit in fire protection could be worthwhile.

Chapter 8 Conclusion

8.1 Brominated Flame Retardants in Museums

At present, it is likely that most museums do not have their own fire protection engineer on staff to advise them about flame retardant plastics and other flame retardant treated materials. These smaller museums also may not have the laboratory facilities and materials to conduct testing very often, so they are likely to rely on the tried-and-true, corrosion-free safety of pure polyethylene, rather than risking the use of a halogenated material. Perhaps the Smithsonian Institution will exercise its authority and influence by conducting the appropriate tests and setting the standard for conservation and fire protection for museums everywhere.

Although the MSDS sheets obtained for the plastics used in this study, rarely reveal the exact flame retardant chemical additives, it is shown that XRF analysis easily confirms the presence of bromine and antimony in the flame retardant plastics, and shows their absence in the polyethylene sheeting. These results support expectations that the FR plastics contain polybrominated diphenyl ethers and antimony oxide, common fire retardants.

The brominated plastics are very controversial at the moment, due to indications that the PBDEs are just as harmful as some of their outlawed counterparts in terms of toxic danger to humans, animals and the environment. This reason alone may discourage the use for this type of FR plastic; however, advances in technology have made the FR additives more stable and more effective, so that smaller amounts of brominated agents

are now being used to reach the same level of flame retardancy. Even so, these plastics might be strictly limited or even banned in the near future, so alternatives will be needed.

The experimental results presented here suggest that the bromine was not easily liberated from the plastics, even after boiling and exposure to heat and humidity. Because it was so difficult to get detectable amounts of the bromine out of the plastics, it may be assumed that in more controlled museum environments, the plastics will probably not off-gas at a rate that will be dangerous to museum objects. Given the overall results, it seems that for the museum environment in particular, the brominated plastics are probably safe to use for short periods of time.

However, more testing is needed, especially in regard to UV exposure, since many plastics begin to breakdown in the presence of UV light. UV exposure is not an issue in the indoor museum environment, but it is still important to understand the mechanisms that can cause the FR plastics to become unstable. More testing is also needed to assess the quality and corrosivity of the smoke of burning FR plastics versus non-FR plastics. Larger scale, better controlled fire tests are also needed to better assess the reduction in probability of fire or flame spread with the use of FR plastics. Finally, more work must be done to develop electrochemical testing for this application, especially in terms of using a wider range of metals, and of test materials. The extraction methodology used to prepare the electrolyte solution for the electrochemical testing needs to be improved in efficiency.

8.2 Oddy Test Improvements

The Oddy test analysis was improved during this experiment by using XRF and XRD analysis of selected coupons to examine the corrosion spots. Instead of relying

solely on visual assessments of the appearance of the coupons, these procedures allowed for the identification of the corrosion. Although the Oddy test results did yield inconsistent corrosion spots, and did not seem to correlate to the materials being tested, the evidence from XRF and XRD analysis did not yield evidence that bromine or antimony reacted with the copper, lead, or silver coupons to any significant degree in the numerous testing protocols. Results show that the Oddy test alone, with visual assessments, can easily lead to incorrect assumptions. All of the corrosion spots formed on the coupons in these tests were oxides or carbonates, which could form in hot and/or moist environments, regardless of the presence of brominated plastics.

8.3 Electrochemical Testing of Exhibit Materials

8.3.1 Benefits of Electrochemical Testing

The electrochemical testing as a method to assess the corrosivity of museum exhibit materials is a far quicker process than the Oddy test, which is currently used in many museums. Once the setup of the cell is complete, the procedure is extremely quick and easy to run. The software is very user-friendly and handles the data formatting, but still allows control from the user.

Very few materials are needed to set up the test beside the actual potentiostat and associated software, which are, however, expensive. The cell was made entirely from objects already in a laboratory, with the exception of the reference electrode. The metal coupons can be reused from test to test by polishing with an abrasive, and the plater's tape was obtained for free as a sample from 3M.

The electrochemical test uses aqueous extracts boiled from the materials being tested. In a sense, this procedure mimics the Oddy test which uses 100% relative

humidity and heat, to drive volatiles from the material in question. The extractions provide a way to transfer the volatiles into a liquid, which can be stored for an extended period of time and used in other tests such as pH measurements.

The results of electrochemical testing are also superior to that of the Oddy test in that they are quantitative. As discussed above, it is not unreasonable to use a rate of corrosion in a risk assessment methodology. Electrochemical testing has been used for years for industrial purposes, looking at how structural elements will corrode when subjected to varying conditions, so that it should be reasonably straightforward to adapt to this application.

8.3.2 Problems with Electrochemical Testing

Although there are many positive aspects that can be ascribed to using the electrochemical testing, there are also a number of deficiencies. For one, in the tests performed in this study, only copper coupons were used. This was not the original intention of the project. As testing went on, and the copper tests were complete, attempts were made to use both lead and silver. The silver gave extremely inconsistent results. The lead was difficult to clean, and the cleaning procedure presented the element of inhaling toxic lead dust. The lead available for testing was also not in the best condition, so it was very difficult to form a good seal in the cell. The water kept leaking out before testing could begin, so the other metals were abandoned, and the focus remained limited to copper.

The repeatability of the tests is also questionable. It would require at least two tests performed by different people to evaluate whether the tests could be repeated under different cell conditions. The extraction procedure was also not ideal, due to the

insolubility of the plastics in water. The extraction itself is the most important element of the test. If the extraction does not accurately represent the tendency of the material to leach and evolve volatiles, then the results are meaningless.

Electrochemical testing is a simple procedure, but the equipment, software and training were very expensive. The uses for the equipment and software are limited, so the benefits gained from this test may not justify the cost. The Oddy test may provide enough information to draw conclusions, without any extra cost.

In conclusion, electrochemical testing has many benefits, but it is important to realize that the method needs further development. Although it may be a long way from becoming a standard museum tool, electrochemical testing shows great promise for use in conservation.

8.4 The Future of Flame Retardants

In conclusion, the question of whether or not flame retardant plastics are appropriate must be assessed on a case by case basis. This study provides an outline of how this problem can be addressed through the use of new data collection methods, and traditional museum risk assessment, tailored to the needs and problems in each individual museum. Although this study only looks at the effects on metals, the overall approach presented here can be used for other risks that involve both fire and contamination.

The flame retardant plastics tested are slightly more corrosive than pure polyethylene, but not as corrosive as plywood or cellulose acetate. The FR plastics are estimated to provide a small amount of reduction in fire risk, but this estimation needs to be assessed with a more specific museum scenario in mind. However, the most pressing issue is the long term life cycle of brominated flame retardants in plastics, which have not

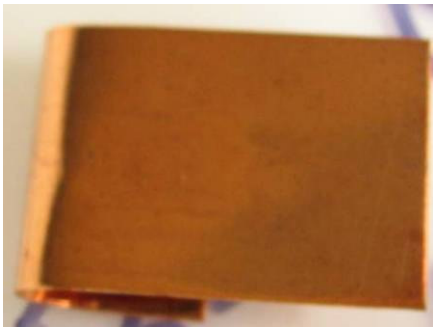
been assessed here, but were touched on in the background research. Flame retardant plastics may slow the spread of fire, but research has shown that they are not good for humans, animals and the environment in general.

In looking at the evidence has as a whole, it seems like the brominated flame retardant plastics are reasonably safe for short term museum use.

It is also possible that better flame retardant plastics will be available in the future. There is a new plastic currently under development – Bishydroxydeoxybenzoin (BDHB). This non-halogenated FR polymer is being developed by a group of scientists from the University of Massachusetts. The plastic releases water vapor when it breaks down in a fire making it "nearly fireproof" while still remaining environmentally (and museum) friendly [51]. A material like this could drastically alter the FR plastic market, and could make the decision of whether or not to go flame retardant very easy. Although it is still years away from being on the market, this type of material represents the future of flame retardant plastics in a world that is increasingly aware of the plight of our environment.

Appendix A Oddy Test

A.1 Coupons after Testing

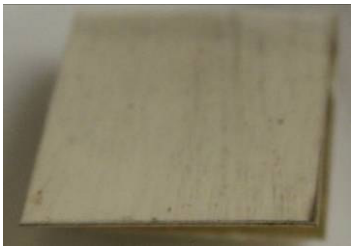


A-1 1. Blank A – Copper

A-1 2. Blank A – Silver

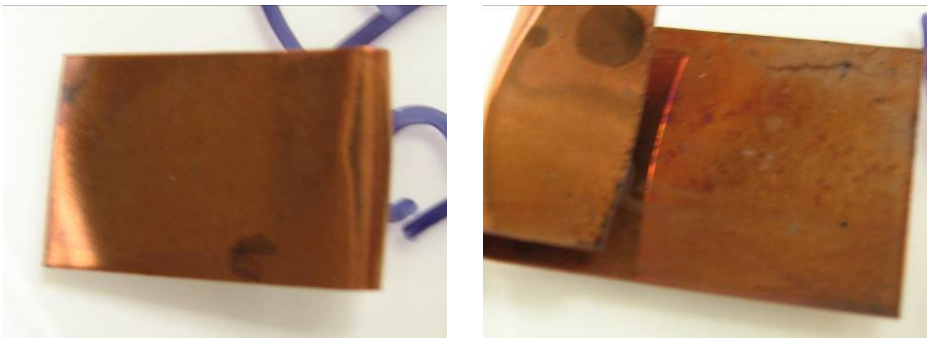
A-1 3. Blank A – Lead

A-1 4. Blank B – Copper

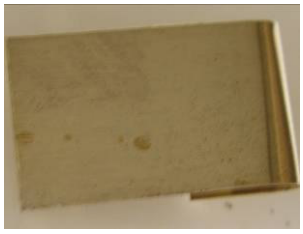


A-1 5. Blank B – Silver

A-1 6. Blank B – Lead

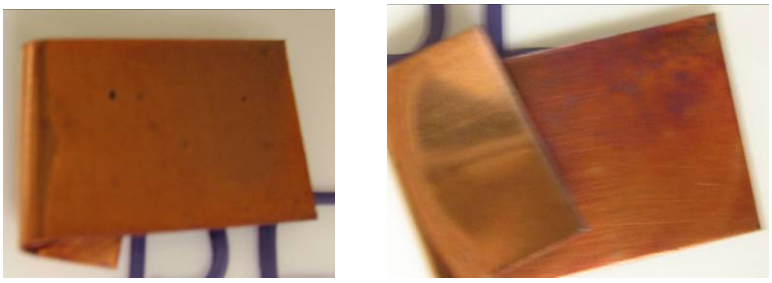


A-1 7. PE A – Copper



A-1 8. PE A – Silver

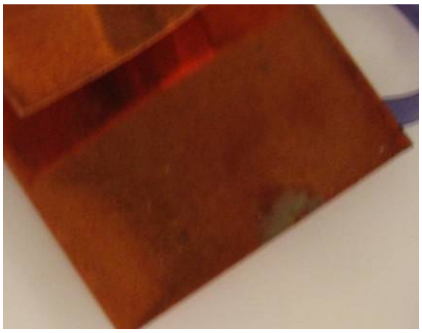
A-1 9. PE A – Lead



A-1 10. PE B – Copper

A-1 11. PE B – Silver

A-1 12. PE B – Lead

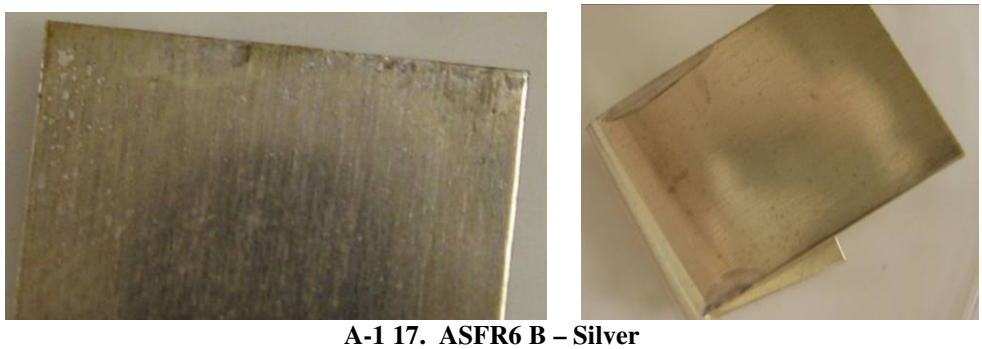


A-1 13. ASFR6 A – Copper

A-1 14. ASFR6 A – Silver

A-1 15. ASFR6 A – Lead

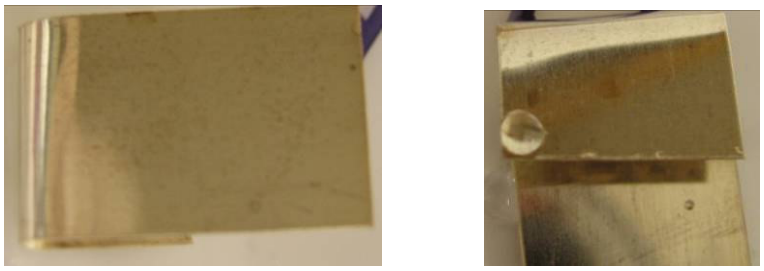
A-1 16. ASFR6 B – Copper



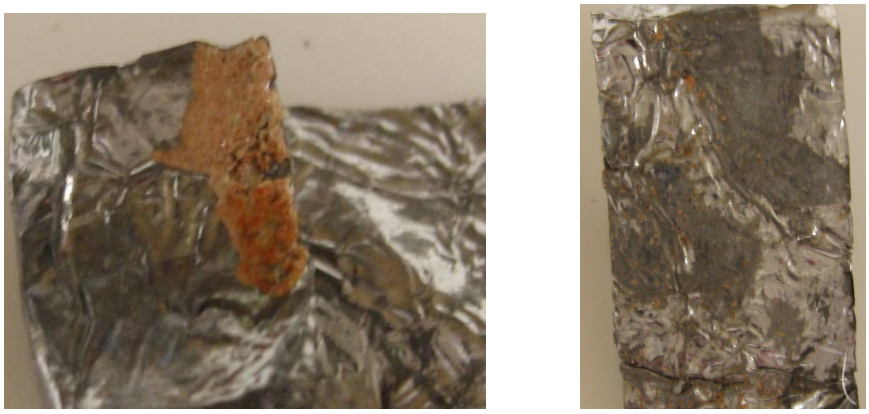
A-1 17. ASFR6 B – Silver

A-1 18. ASFR6 B – Lead

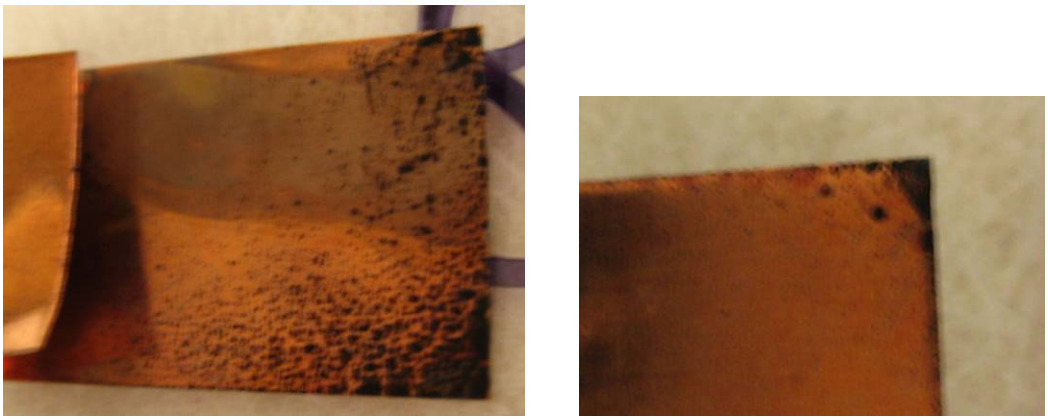
A-1 19. Blue A – Copper



A-1 20. Blue A – Silver



A-1 21. Blue A – Lead

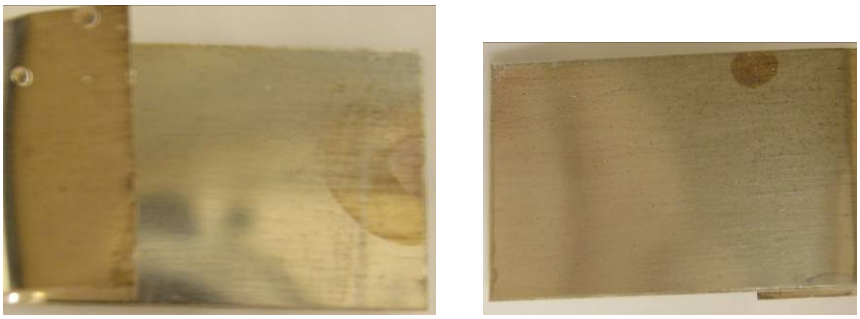


A-1 22. Blue B – Copper

A-1 23. Blue B – Silver

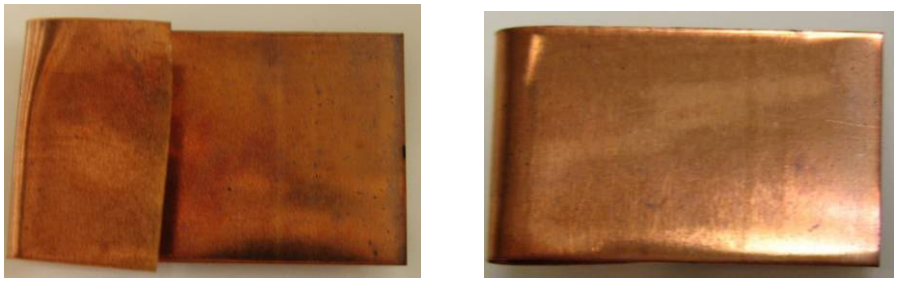
A-1 24. Blue B – Lead

A-1 25. DS2FR A – Copper

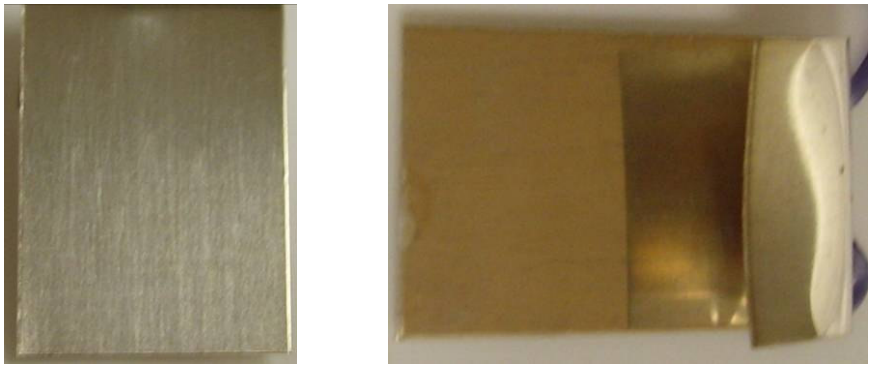


A-1 26. DS2FR A – Silver

A-1 27. DS2FR A – Lead

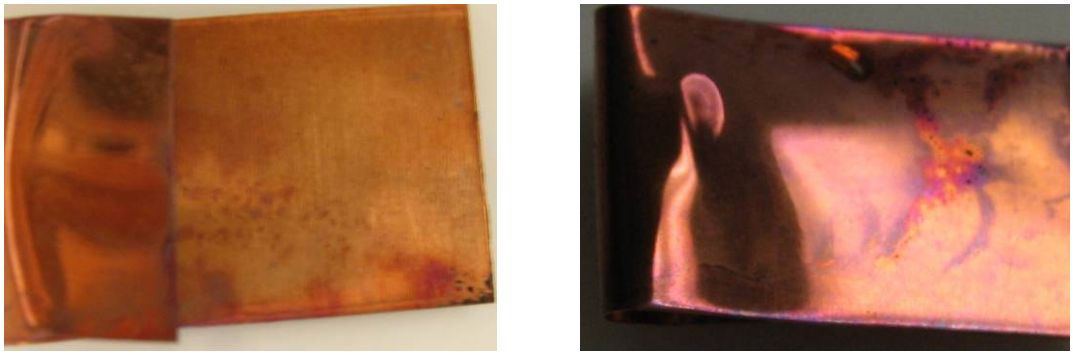


A-1 28. DS2FR B – Copper

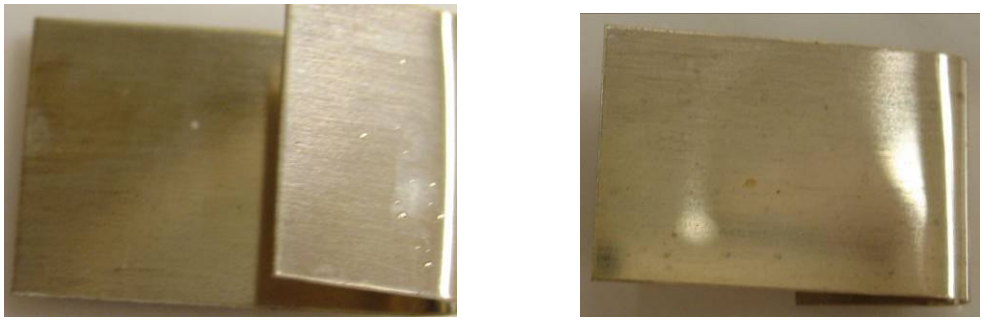


A-1 29. DS2FR B – Silver

A-1 30. DS2FR B – Lead

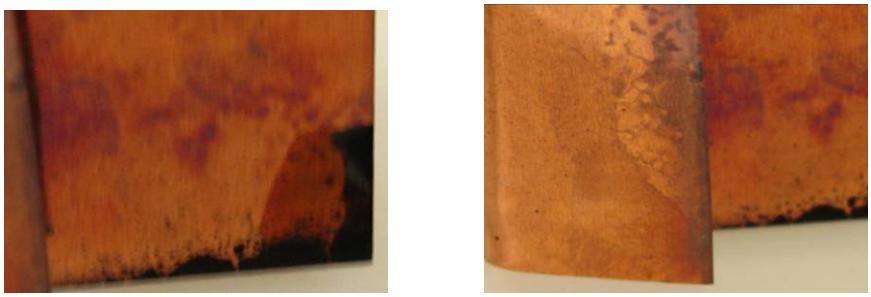


A-1 31. Black A – Copper

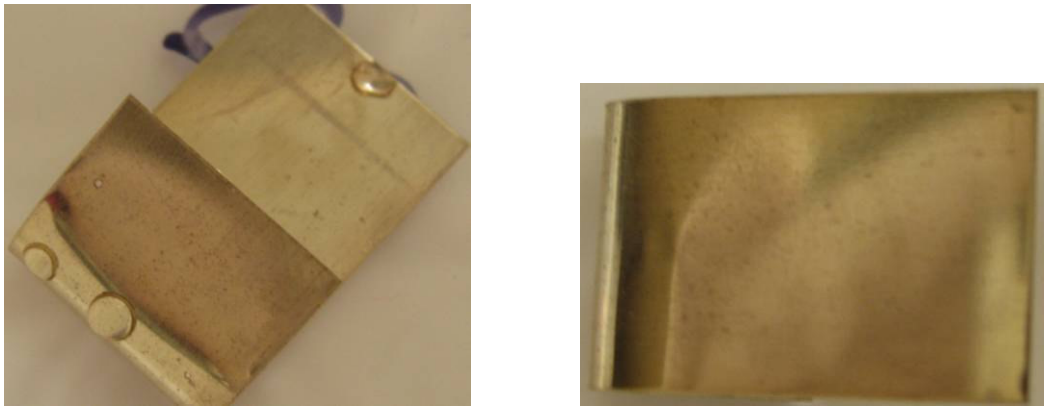


A-1 32. Black A – Silver

A-1 33. Black A – Lead



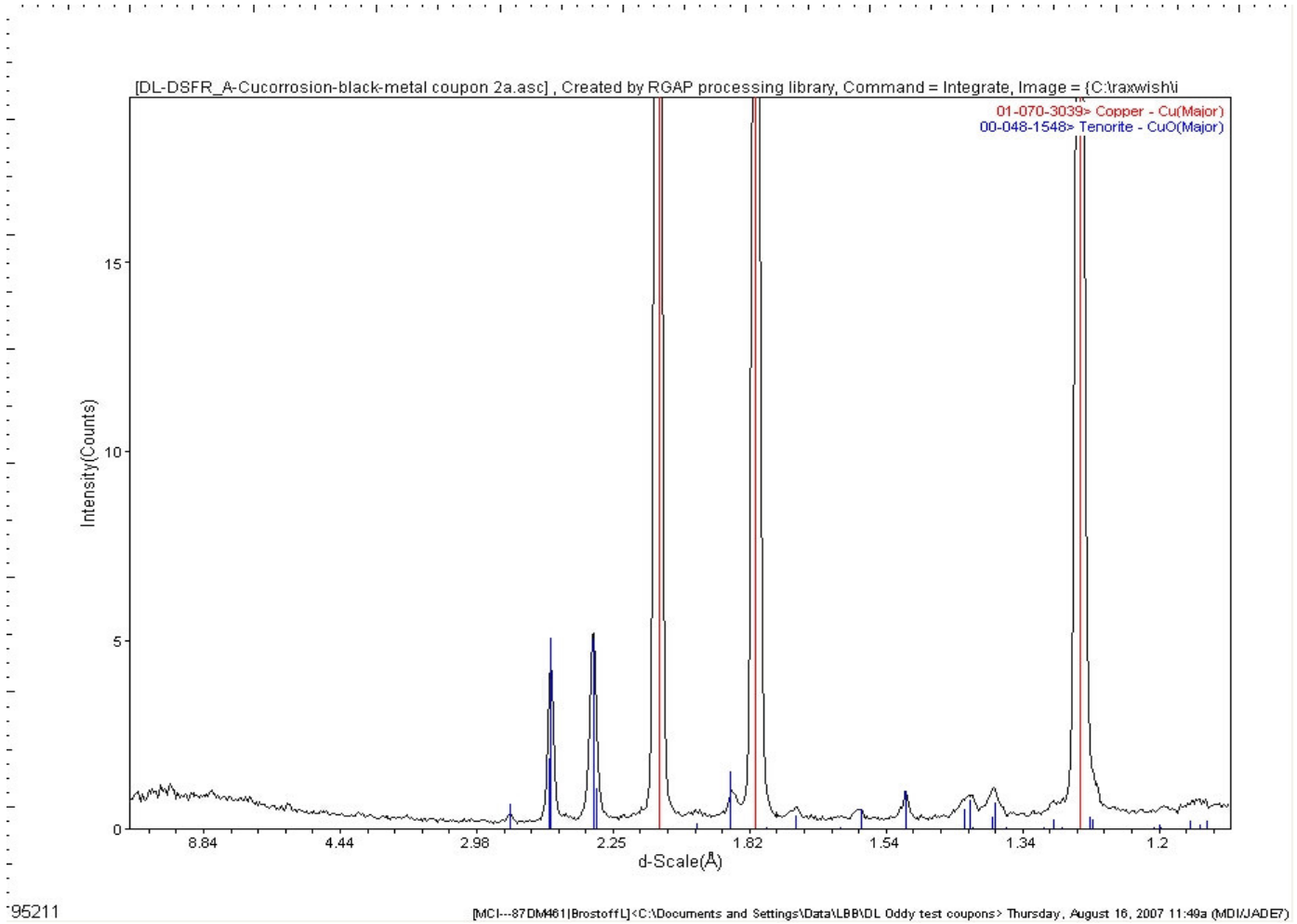
A-1 34. Black B – Copper



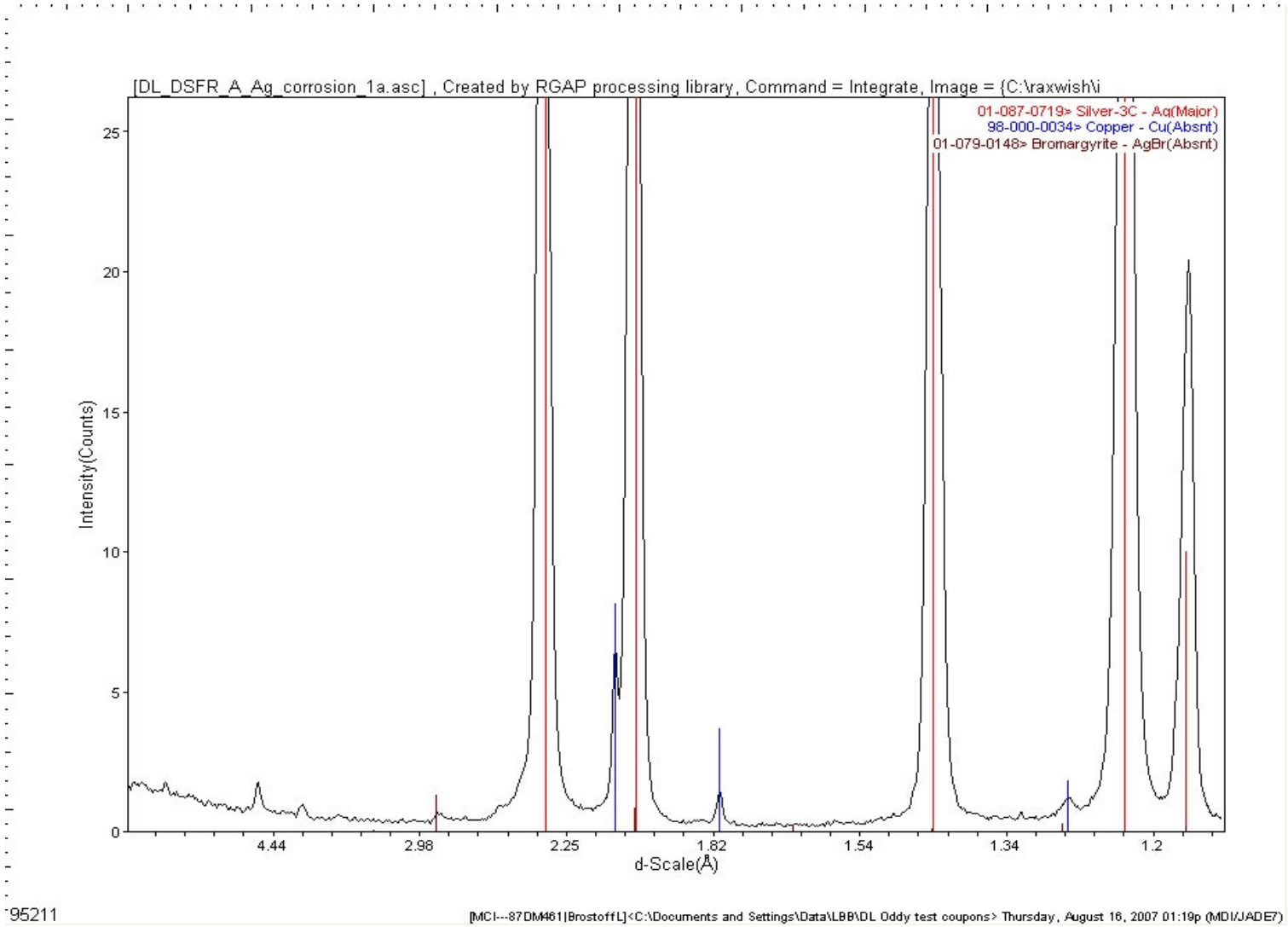
A-1 35. Black B – Silver

A-1 36. Black B – Lead

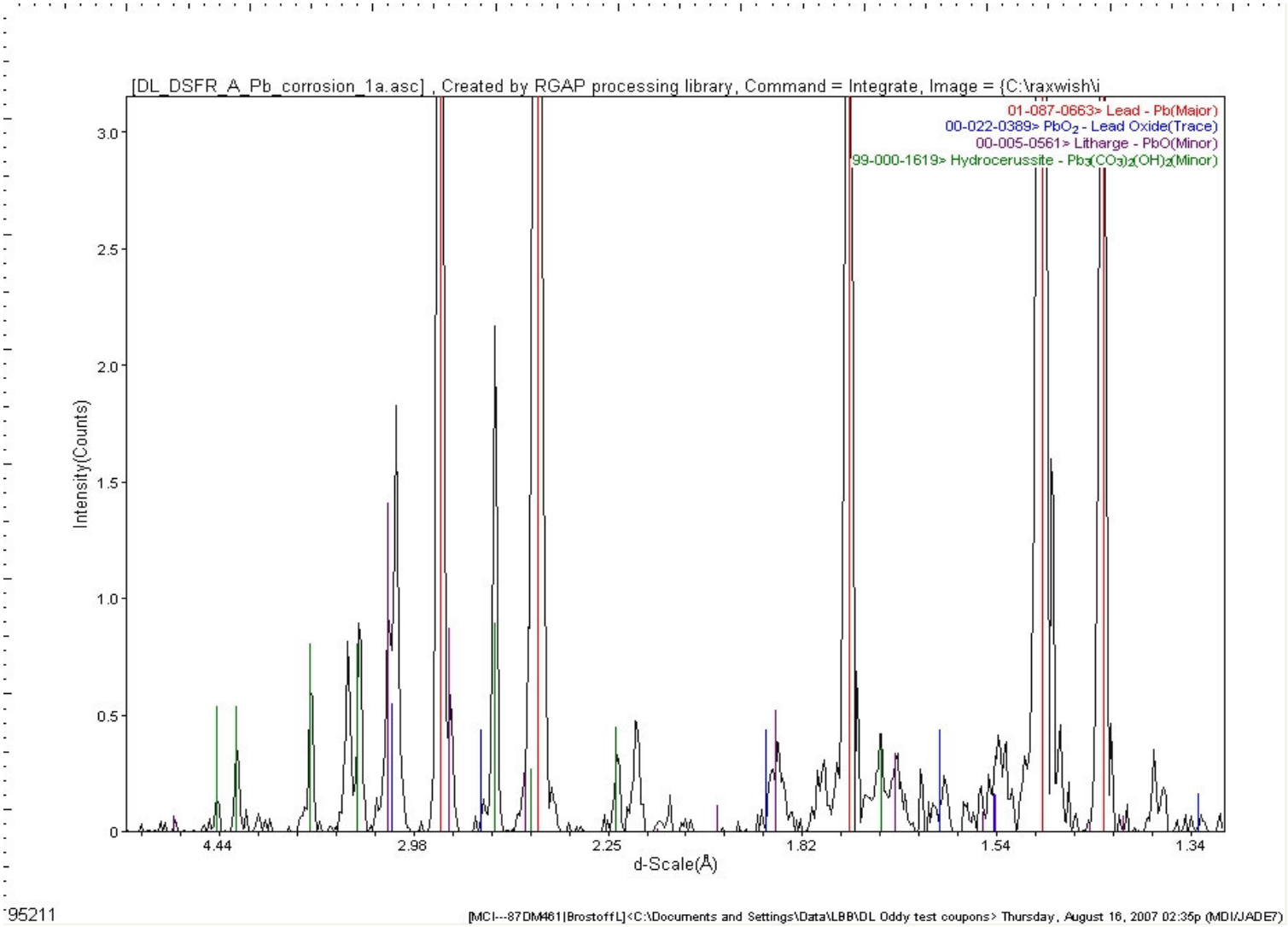
A.2 XRD



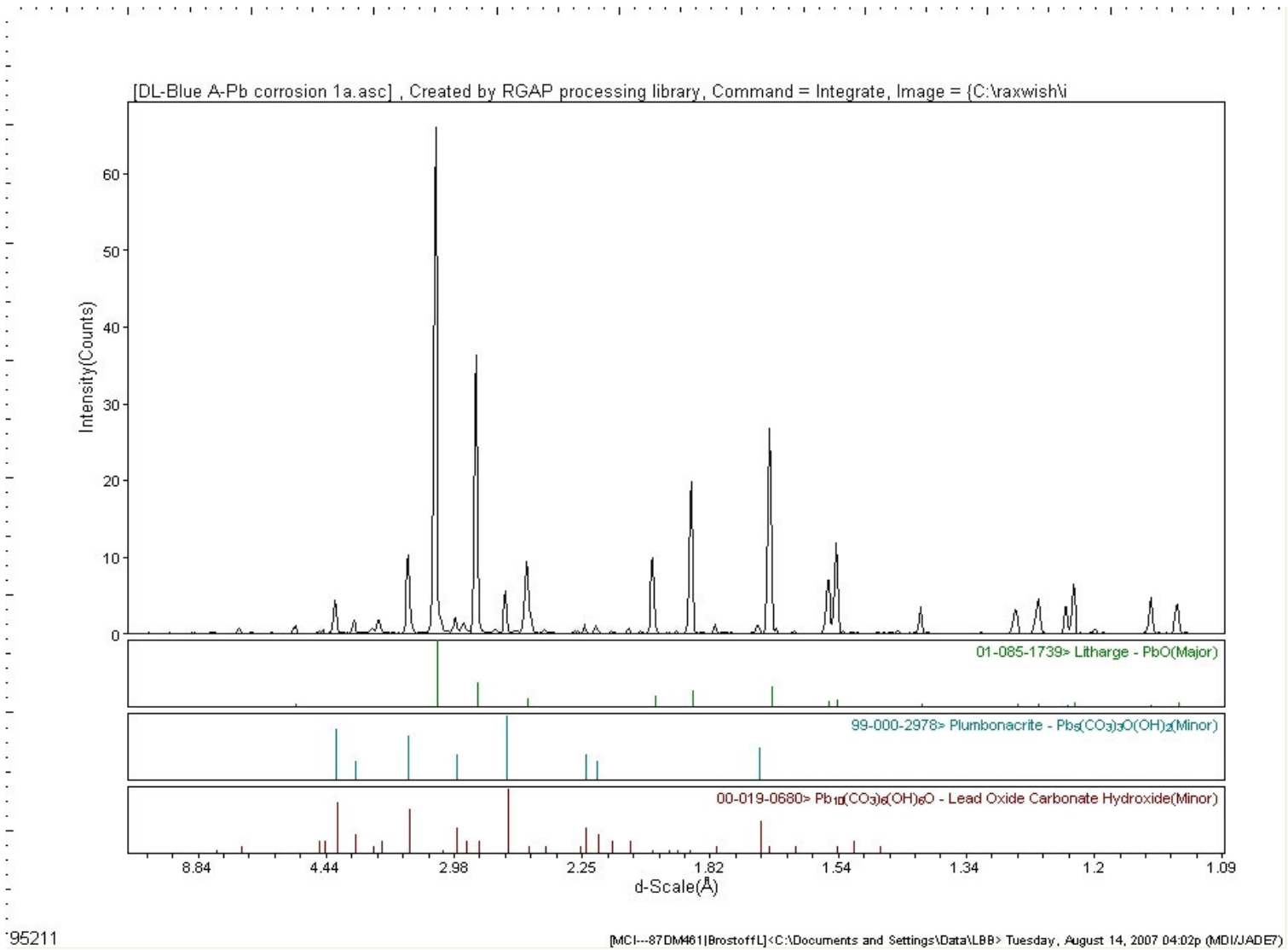
A.2-1. DSFR A Oddy test coupon: Copper.



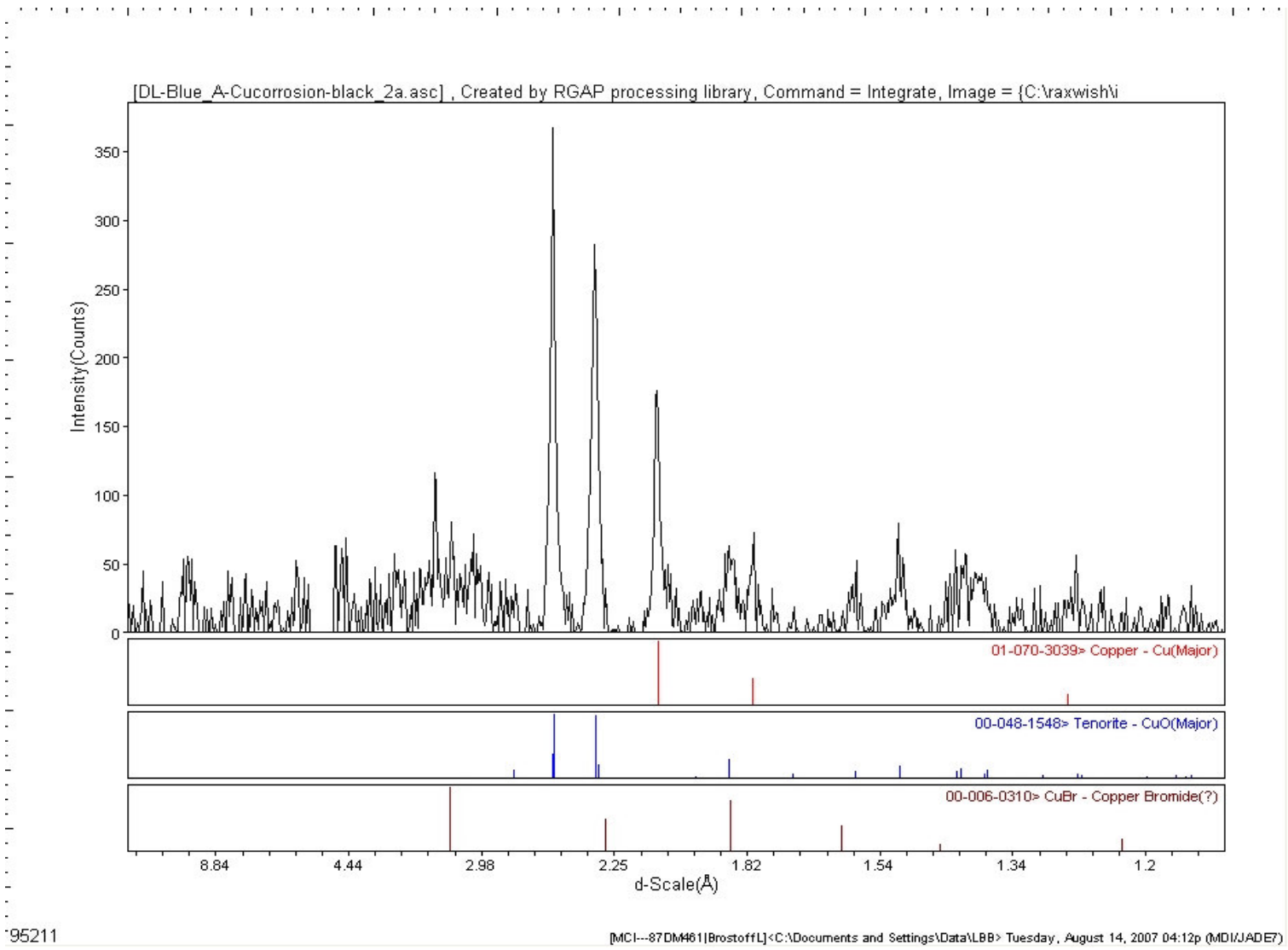
A.2-2. . DSFR A Oddy test coupon: Silver.



A.2-3. . DSFR A Oddy test coupon: Lead.



A.2-4. . Blue A Oddy test coupon: Lead.



A.2-5. . Blue A Oddy test coupon: Copper.

Appendix B Charts

Mark with X in appropriate box.			Color Change/Overall Corrosion						% Area Corrosion (Spots)						
			1	2	3	4	5				1	2	3	4	5
			None	Slight	Medium	Fair Amount	Dramatic				None 0%	1-10%	11-20%	21-30%	>30%
Please rate on a scaled from 1-5, 1 being the best condition compared to the clean sample, 5 being the worst condition compared to the clean sample. Ratings are taken in reference to the overall corrosion, generally seen in color change (Column 1), and in spots of corrosion, rated by the percentage of the total area covered by spots (Column 2).	Blank A	Cu							Blank A	Cu					
		Ag								Ag					
		Pb								Pb					
	Blank B	Cu							Blank B	Cu					
		Ag								Ag					
		Pb								Pb					
	PE A	Cu							PE A	Cu					
		Ag								Ag					
		Pb								Pb					
	PE B	Cu							PE B	Cu					
		Ag								Ag					
		Pb								Pb					
	ASFR A	Cu							ASFR A	Cu					
		Ag								Ag					
		Pb								Pb					
	ASFR B	Cu							ASFR B	Cu					
		Ag								Ag					
		Pb								Pb					
	Blue A	Cu							Blue A	Cu					
		Ag								Ag					
		Pb								Pb					
	Blue B	Cu							Blue B	Cu					
		Ag								Ag					
		Pb								Pb					
	DSFR A	Cu							DSFR A	Cu					
		Ag								Ag					
		Pb								Pb					
	DSFR B	Cu							DSFR B	Cu					
		Ag								Ag					
		Pb								Pb					
	Black A	Cu							Black A	Cu					
		Ag								Ag					
		Pb								Pb					
	Black B	Cu							Black B	Cu					
		Ag								Ag					
		Pb								Pb					

B 1. Chart given for others to rate the coupons following the Oddy test.

Agent of Deterioration	Type of Risk	Example of Risk	Levels for Control: location	site	building	room	cabinet	specimen	policy	procedure
Physical forces	1	earthquake								
	2	mishandling								
	3	poor support								
Fire	1									
Water	1	flood								
	2	roof leaks								
	3	rising damp								
Criminals	1	major theft								
	2	isolated vandalism								
	3	embezzlement by staff								
Pests	2	infestation								
Pollutants	1	from nearby disaster								
	2	corrosive cleaner used								
	3	wooden storage materials								
Light and radiation	3	exposure to light								
Incorrect temperature	2	thermal shock								
	3	higher than ideal								
Incorrect relative humidity	2	HVAC malfunction								
	3	higher (or lower) than ideal								
Custodial neglect	1	collection abandonment								
	2	loss of specimen data								
	3	lack of legal title								

least important ▢ ▢ ▢ ▢ most important

B 2. "Specific examples of types of reisk and the relative importance of implementing means of control at each possible level for control. Type of risk: 1 = catastrophic, 2 = severe, and 3 = mild/gradual [13]."

Appendix C Burn Test Notes & Observations

Thermocouples
TC 1 – I 0110
13.5 in. above top of statue
23.5 in. above base

TC 2 – BF 0109
TC wire goes through statue, pokes out under plastic (between tinfoil and plastic)

ASFR6 – Test 2
5/21/07

- 39" x 25" sheet of plastic
- Ignition was very difficult to achieve
- After applying flame a few times, did burn for a while
- (time from video?)
- Mostly the dripped plastics which were deposited around the base and on the tinfoil burned rather than the actual draped plastic
- The plastic seemed to shrink to the monkey shape.
- TC2 poked hole through plastic
- Plastic was very melted to some of the artifact
- Overall: Difficult to ignite with lighter, slow burning, often self extinguishing
- Temperature Data

DS2FR – Test 1
5/21/07

- Faster burning than ASFR6, self extinguishes after a while.
- Difficult to get going
- Gets very hard when cools after self extinguishing; sticks to artifact (almost solid!)

DS2FR Test 2

- Less burning occurred in this test, so the metal samples are "clean" but were exposed to fumes briefly.
- Need to check out video for actual burn times
- Need to look at temperatures reached under plastic to see what was going on and draw some possible conclusions about smoke.

BlackFR – Test 1
5/24/07

- 4 mil thickness
- 36" x 24"
- Really hard to ignite

- Once ignited and then cooled into solid, is nearly impossible to reignite (note the thin strip that formed and shrunk together, to no longer ignite)
- Seemed to be putting out the lighter even! (maybe lighter got plastic goo inside)
- Seems to shrink away from heat without igniting.
- Drips and solidified/melted and cooled plastic parts are very hard, stuck to artifact.

Black FR – Test 2

- 35" x 24"
- If plastic drips on itself, we get more fire, faster spreading
- At one point, a pool of drips on artifact burned in a sustained fashion
- The hardened already burned and cooled bits seem to be even more difficult to reignite (potentially impossible with small flame)
- The drips are very thick and gooey; tar like
- The black color is a potential issue – is this material available in clear or is ASFR6 a comparable alternative in the milky-clear color?

Polyethylene – Test 3

- 24" x 30"
- This time, not in the corner configuration as the first two tests
- Just draped over, as the other plastics were.
- Started temperature read halfway into fire.
- PE melted and pool fires burned for really long time
- Very fast fire
- Spread from single ignition point to entire covering
- Lead melts away completely from the heat produced
- Clearly hotter, larger, more easily ignitable than any of the FR plastics.

Blue Deck cover – Test 1

- Very thick plastic (doesn't conform to shape very well and would be better suited as a separation barrier for construction)
- Burned up corner in 7 seconds, extinguished
- Sustained a small flame for 56 seconds then self extinguished: this was upward spread, and at a spot where ignition had already been attempted/smoldering had occurred
- Burning drips – the drippings burn longer than the sheets; they sit in a pool
- The flames flicker and flash

Blue Deck cover – Test 2

- Does not shrink up like other FR plastics
- Will sustain flames for approximately 1 minute, then extinguishes
- When burning, produces lots of smoke

Bibliography

1. Waller, R., *Conservation Risk Assessment: A Strategy for Managing Resources for Preventive Conservation*, in *Preventive Conservation Practice, Theory and Research. Preprints of the Contributions to the Ottawa Congress*. 1994, International Institute for the Conservation of Historic and Artistic Works: London. p. 12-16.
2. Farhi, P., *Committee Sees a Lack of Money, Leadership at 8 Smithsonian Museums*, in *Washington Post*. March 21, 2007: Washington, DC.
3. Tetreault, J. *Display Materials: The Good, the Bad and the Ugly*. in *The Scottish Society for Conservation and Restoration*. 1994. Edinburg, Scotland.
4. Wilson, J.A., *Fire Protection in Cultural Institutions*, in *The 17th Annual National Archives and Records Administration (NARA) Preservation Conference: Lessons Learned in Emergencies: Not Your Ordinary Disaster Conference*. 2002, National Archives & Records Administration: College Park, MD.
5. Dufton, P., *Flame Retardants for Plastics Market Report*. July 2003, Rapra Technologies Limited: Shawbury, Shrewsbury, Shropshire.
6. Birnbaum, L.S. and D.F. Staskal, *Brominated Flame Retardants: Cause for Concern?* Environmental Health Perspectives, 2004. **112**(1): p. 9-17.
7. Lomakin, S.M. and G.E. Zaikov, *Modern Polymer Flame Retardancy*. New Concepts in Polymer Science. 2003, Zeist, The Netherlands: Brill Academic Publishers.
8. Bamberger, J., E.G. Howe, and G. Wheeler, *A Variant Oddy Test Procedure for Evaluating Materials Used in Storage and Display Cases.* Studies in Conservation, 1999. **44**(2): p. 86-90.
9. Bamberger, J., *The Oddy Test Improved.* Met Objectives, 2003. **4**(2): p. 4.
10. Reedy, C., R. Corbett, and M. Burke, *Electrochemical Tests as Alternatives to Current Methods for Assessing Effects of Exhibition Materials on Metal Artifacts.* Studies in Conservation, 1998. **43**(3): p. 183-196.
11. *Annex B Fire Experience in Cultural Resource Properties*, in *NFPA 909 Protection of Cultural Resource Properties - Museums, Libraries, and Places of Worship*. 2005, NFPA.
12. Freeland, D. *Fire Protection 201*. in *1999 National Conference on Cultural Property Protection Proceedings: Cultural Property Protection from the Ground Up*. 1999. Washington, DC: National Conference on Cultural Property Protection.
13. Waller, R., *Risk Management Applied to Preventive Conservation*, in *Storage of Natural History Collections: A Preventive Conservation Approach*. 1995, Society for the Preservation of Natural History Collections: Iowa City. p. 21-27.
14. Waller, R., *Preventive Conservation Planning for Large and Diverse Collections*. 1996, American Institute for Conservation.
15. Oddy, W.A., *An Unsuspected Danger in Display.* Museum Journal, 1973. **73**(1): p. 27-29.
16. Daniels, V. and S. Ward, *A Rapid Test for the Detection of Substances Which Will Tarnish Silver.* Studies in Conservation, 1982. **27**(2): p. 58-60.
17. Bernt, H., *Measuring the Rate of Atmospheric Corrosion in Microclimates.* Journal of the American Institute for Conservation, 1990. **29**(2): p. 207-220.

18. Green, L.R. and D. Thicket, *Modern Metals in Museum Collections*, in *Saving the Twentieth Century: The Conservation of Modern Materials*, D. Grattan, Editor. 1991, Communications Canada: Ottawa, Canada. p. 261-272.
19. Zhang, J., D. Thicket, and L.R. Green, *Two Tests for the Detection of Volatile Organic Acids and Formaldehyde.* Journal of the American Institute for Conservation, 1994. **33**(1): p. 47-53.
20. Green, L.R. and D. Thicket, *Testing Materials for Use in Storage and Display of Antiquities: A Revised Methodology.* Studies in Conservation, 1995. **40**(3): p. 145-152.
21. Siebert, O.W., *Laboratory Electrochemical Test Methods*, in *Laboratory Corrosion Tests and Standards*, G.S. Haynes and R. Baboian, Editors. 1985, ASTM: Philadelphia, PA. p. 65-90.
22. Berke, N.S. and M.C. Hicks, *Electrochemical Methods of Determining the Corrosivity of Steel in Concrete*, in *Corrosion Testing and Evaluation: Silver Anniversary Volume*, R. Baboian and S.W. Dean, Editors. 1990, ASTM: Philadelphia, PA. p. 425-450.
23. *ASTM G59-97 Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements*. 1998, ASTM: West Conshohocken, PA. p. 237-240.
24. *ASTM G3-89 Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing*. 1999, ASTM: West Conshohocken, PA. p. 40-47.
25. *ASTM G5-94 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*. 1999, ASTM: West Conshohocken, PA. p. 58-69.
26. *ASTM G102-89 Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements*. 1999, ASTM: West Conshohocken, PA. p. 432-438.
27. *ASTM C871-95 Standard Test Method for Chemical Analysis of Thermal Insulation of Materials for Leachable Chloride, Fluoride, Silicate and Sodium Ions*. 2000, ASTM: West Conshohocken, PA. p. 432-436.
28. Lindemann, R.F., *Flame Retardants for Polystyrene.* Industrial and Engineering Chemistry, 1969. **61**(5): p. 70-75.
29. Hastie, J.W., *Treasures of the Past VIII: Molecular Basis of Flame Inhibition (1973).* Journal of Research of the National Institute of Standards and Technology, 2001. **106**(4): p. 731-752.
30. Nametz, R.C., *Bromine Compounds for Flame Retarding Polymer Compositions*, in *Flame Retardancy Advances in Fire Safety: Regulations, Testing, Products, Markets*. 1984, Fire Retardant Chemicals Association: Pine Mountain, Georgia.
31. Babrauskas, V., *The Effects of FR Agents on Polymer Performance*, in *Heat Release in Fires*, V. Babrauskas and S.J. Grayson, Editors. 1992, Elsevier Applied Science Publishers: London. p. 423-446.
32. Georlette, P., *Applications of halogen Flame Retardants*, in *Fire Retardant Materials*, A.R. Horrocks and D. Price, Editors. 2001, Woodhead Publishing Limited: Cambridge, England. p. 264-292.

33. Lewin, M. and E.D. Weil, *Mechanisms and modes of action in flame retardancy of polymers*, in *Fire Retardant Materials*, A.R. Horrocks and D. Price, Editors. 2001, Woodhead Publishing Limited: Cambridge. p. 31-68.
34. Price, D., G. Anthony, and P. Carty, *Introduction: polymer combustion, condensed phase pyrolysis and smoke formation*, in *Fire Retardant Materials*, A.R. Horrocks and D. Price, Editors. 2001, Woodhead Publishing Limited: Cambridge. p. 1-28.
35. Purser, D., *Toxicity of fire retardants in relation to life safety and environmental hazards*, in *Fire Retardant Materials*, A.R. Horrocks and D. Price, Editors. 2001, Woodhead Publishing Limited: Cambridge, England. p. 69-123.
36. Alaee, M. and R.J. Wenning, *The significance of brominated flame retardants in the environment: current understanding, issues and challenges.* Chemosphere, 2002(46): p. 579-582.
37. *An Introduction to Brominated Flame Retardants*. 2000, Bromine Science and Environmental Forum: Brussels, Belgium.
38. Tullo, A.H., *Plastic Additives' Steady Evolution.* Chemical & Engineering News, 2000. **78**(49): p. 21-31.
39. de Wit, C.A., *An overview of brominated flame retardants in the environment.* Chemosphere, 2002. **46**: p. 583-624.
40. Tange, L. and R. Montaigne, *New Study Demonstrates Compatibility of Brominated Flame Retardant Plastics with Feedstock Recycling and Energy Recovery Process*. 2003, European Brominated Flame Retardant Industry Panel: Brussels.
41. Rademakers, P., W. Hesseling, and J. van de Wetering, *Review on Corrosion in Waste Incinerators and Possible Effect of Bromine*. 2002, Netherlands Organisation for Applied Scientific Research (TNO).
42. Darnerud, P.O., *Toxic Effects of Brominated Flame Retardants in Man and in Wildlife.* Environmental International, 2003. **29**: p. 841-853.
43. D'Silva, K., A. Fernandes, and M. Rose, *Brominated Organic Micropollutants - Igniting the Flame Retardant Issue.* Critical Reviews in Environmental Science and Technology, 2004. **34**: p. 141-207.
44. Hites, R.A., *Brominated Flame Retardants in the Environment.* Journal of Environmental Monitoring, 2005. **7**(11): p. 1033-1036.
45. Masten, S.A., *Antimony Trioxide: Brief Review of Toxicological Literature*, N.T. Program, Editor. 2005, Nation Institute of Environmental Health Sciences, National Institute of Health: Research Triangle Park, NC.
46. *Bromine Science and Environmental Forum (BSEF).* [cited; Available from: www.bsef.com.
47. *Toxicological Risks of Selected Flame-Retardant Chemicals*. in *Subcommittee on Flame-Retardant Chemicals, Committee on Toxicology, Board on Environmental Studies and Toxicology, National Research Council*. 2000. Washington, DC: The National Academies Press.
48. *Gamry Instruments Application Notes*. 2007 June 28, 2007 [cited; Available from: www.gamry.com/App%5FNotes/Index.htm.
49. Doelling, R. *Potentiostats*. 2000 July 6, 2007 [cited; Available from: www.bank-ic.de/encms/downloads/potstae2.pdf.

50. *American Association of Museums*. 2007 [cited 2007; Available from: http://www.aam-us.org.
51. Antosiewicz, F. *UMass Scientist Unveil Fire-Safe Polymer*. Plastic News June 18, 2007 [cited; Available from: www.plasticnews.com.